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# Ammonia Absorption/Ammonium Bisulfate Regeneration Pilot Plant for Flue Gas Desulfurization

Tennessee Valley Authority, Muscle Shoals, Ala

Prepared for

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The report gives results of a pilot-plant study of the ammonia absorption/ammonium bisulfate regeneration process for removing $SO_2$ from the stack gas of coal-fired power plants. Data were developed on the effects of such operating variab in the absorption of $SO_2$ by ammoniacal liquor as: temperature and flyash content of inlet flue gas, pH of recirculating absorber liquor, and oxidation of sulfite to sulfate in absorber liquor. An equation was developed for operating conditions that should pr vent fume formation in the absorber; however, consistent plumeless pilot-plant operation was not achieved. Acidulating and stripping equipment and operating conditions were developed for recovering 99+ % of the $SO_2$ in the absorber product liquor as a gas of suitable concentration for processing to sulfuric acid or elemental sulfur. The proposed study of electrical decomposition of ammonium sulfate to recover ammonia and ammonium bisulfate for recycling was not undertaken because of indicated high energy requirements and unfavorable economics. It is recommended that any further work involving $SO_2$ removal with ammonia be directed toward a noncyclic process with production of ammonium sulfate.

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| Flue Gases, Coal, Combustion, Ammonia | Stationary Sources | 21B 21D -- 07 |
| Sulfur Dioxide, Desulfurization | Ammonium Bisulfate | -- 07A,07D |
| Absorption, Regeneration (Engineering) | $SO_2$ Absorption | 14B -- |
| Sulfuric Acid, Sulfur, Ammonium Sulfate | Sodium Sulfite Slurry | |
| Slurries, Limestone, Magnesia | Plume Opacity | 11G 08G -- |

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# AMMONIA ABSORPTION/AMMONIUM BISULFATE REGENERATION PILOT PLANT FOR FLUE GAS DESULFURIZATION

by

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# ABSTRACT

A pilot-plant study was made of the ammonia absorption - ammonium bisulfate regeneration (ABS) process for removing $SO_2$ from the stack gas of coal-fired power plants. Data were developed on the effects of operating variables in the absorption of $SO_2$ by ammoniacal liquor; variables included temperature and flyash content of inlet flue gas, pH of recirculating absorber liquor, and oxidation of sulfite to sulfate in absorber liquor. An equation was developed for operating conditions that should prevent fume formation in the absorber; however, consistent plumeless pilot-plant operation was not achieved. Acidulating and stripping equipment and operating conditions were developed for recovering 99+% of the $SO_2$ in the absorber product liquor as a gas of suitable concentration for processing to sulfuric acid or elemental sulfur. The proposed electrical decomposition of ammonium sulfate to recover ammonia and ammonium bisulfate for recycling in the process was not studied because of indicated high energy requirements and unfavorable economics. Recommendation is made that any further work involving $SO_2$ removal with ammonia be directed toward a noncyclic process with production of ammonium sulfate.

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## GLOSSARY, ABBREVIATIONS, UNITS, AND CONVERSION FACTORS

### GLOSSARY

A value: The mols of ammonium sulfate present in solution per 100 mols of total water.

$C_A$ value: The mols of ammonia present in solution in the form of ammonium sulfite and bisulfite (active ammonia) per 100 mols of total water.

Free water: The water of solution contained in the absorbing liquor.

Fume: A suspension of particles in air or gas that may be formed in various ways (condensation or chemical reaction) inside the absorber.

Plume: The gaseous effluent from the pilot-plant stack containing the fume, flyash, and water vapor.

Plume opacity: The percent of light that is obscured in passing through an aerosol plume, dust, or smoke.

Reaction water: The water used in forming ammonium sulfite, bisulfite, and sulfate (1 mol of water used per 1 mol of sulfur).

S value: The mols of $SO_2$ present in solution in the form of ammonium sulfite and bisulfite per 100 mols of total water.

$S/C_A$ value: The mol ratio of the $SO_2$ present as ammonium sulfite and bisulfite to the ammonia present as ammonium sulfite and bisulfite.

Steam plume: That portion of a plume (water) that results when the temperature of the mixed flue gas and ambient air falls below the dew point temperature.

Total water: The free water plus the reaction water (water of constitution) required when $SO_2$ and $NH_3$ react to form ammonium sulfite, bisulfite, and sulfate; 1 mol of water is consumed for each mol of $SO_2$ that reacts.

## ABBREVIATIONS

| | |
|---|---|
| ABS | ammonia absorption - ammonium bisulfate regeneration process |
| Btu | British thermal unit |
| EPA | Environmental Protection Agency |
| FGD | flue gas desulfurization |
| FRP | fiberglass reinforced plastic |
| L/G | the ratio of the liquor flow rate to the gas flow rate |
| NAPCA | National Air Pollution Control Administration |
| SS | stainless steel |
| TVA | Tennessee Valley Authority |
| k | reaction constant |
| $\Delta P$ | pressure differential |
| CPVC | chlorinated polyvinyl chloride |

## UNITS

### Length

| | |
|---|---|
| in. | inch |
| ft | feet, foot |
| $\mu$ | micron, $10^{-6}$ meter |
| cm | centimeter |
| m | meter |
| mm | millimeter |

### Area

| | |
|---|---|
| $in^2$ | square inch |
| $ft^2$ | square foot, feet |

### Volume

| | |
|---|---|
| $in^3$ | cubic inch |
| $ft^3$ | cubic feet, foot |
| gal | gallon |
| ml | milliliter |
| l | liter |
| $cm^3$ | cubic centimeter |
| $m^3$ | cubic meter |

### Mass

| | |
|---|---|
| lb | pound |
| g | gram |
| kg | kilogram |
| gr | grain |

### Time

| | |
|---|---|
| sec | second |
| min | minute |
| hr | hour |

### Temperature

| | |
|---|---|
| °C | degree Celsius |
| °F | degree Fahrenheit |
| °K | degree Kelvin |
| °R | degree Rankine |

### Concentration

| | |
|---|---|
| lb/ft$^3$ | pounds per cubic foot |
| ml/m$^3$ | milliliters per cubic meter |
| g/l | grams per liter |
| ppm | parts per million |
| gr/scf | grains per standard cubic foot |

### Linear velocity

| | |
|---|---|
| ft/sec | feet per second |

### Volumetric flow

| | |
|---|---|
| ft$^3$/min | cubic feet per minute |
| gpm | gallons per minute |
| acfm | actual cubic feet per minute |
| scfm | standard cubic feet per minute |

### Power

| | |
|---|---|
| kW | kilowatt |
| MW | megawatt |

CONVERSION FACTORS

| To convert from English units | To metric units | Multiply by |
|---|---|---|
| ft³/min | m³/min | 0.0283 |
| °F | °C | subtract 32 and multiply by 5/9 |
| Btu/(lb)(°F) | gcal/(g)(°C) | 1 |
| Btu/(hr)(ft²)(°F) | gcal/(sec)(cm²)(°C) | 0.000135 |
| inch | cm | 2.54 |
| oz/ft³ | g/l | 0.00229 |
| gpm | l/sec | 0.0631 |
| mol/(min)(ft²) | mol/(min)(cm²) | 929.03 |
| psi | mm of Hg at 0°C | 51.715 |
| lb/hr | kg/hr | 0.453 |
| ft | m | 0.305 |
| gal/(hr)(ft²) | l/(hr)(m²) | 40.75 |
| ft³ | l | 28.32 |

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We are particularly indebted to Julius Silverberg for his expertise in the organization and writing of technical reports. Mr. Silverberg helped us to incorporate the suggestions of all our reviewers into a more effective report.

# AMMONIA ABSORPTION/AMMONIUM
# BISULFATE REGENERATION PILOT PLANT
# FOR FLUE GAS DESULFURIZATION

## EXECUTIVE SUMMARY

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### INTRODUCTION

This report covers a pilot-plant study carried out by the Tennessee Valley Authority (TVA) for the U.S. Environmental Protection Agency (EPA), under Interagency Agreement EPA-IAG-D4-0361 (TV-31990A), on a cyclic process for removing sulfur dioxide from power plant stack gas. The process, called the ammonia absorption - ammonium bisulfate regeneration process (ABR), consists in (1) scrubbing the flue gas with aqueous ammonia to form ammonium sulfite - ammonium bisulfite solution, (2) acidulating this solution with ammonium bisulfate to release the sulfur dioxide for recovery as a salable product, and (3) thermally decomposing the resultant ammonium sulfate to regenerate ammonium bisulfate for use in the acidulation step and to release ammonia for recycling to the absorber. The study was made in a pilot plant designed to handle about 4,000 acfm (300°F) of stack gas. This amount normally results from the production of about 1.25 MW of electricity in a coal-fired power plant. The pilot plant was located at TVA's Colbert Steam Plant in northwest Alabama and used stack gas from that plant.

### PILOT-PLANT STUDY

The work was carried out in three periods or phases. Phase I (1969-71) was initiated to gain engineering information on ammonia ($NH_3$) absorption of sulfur dioxide ($SO_2$) when applied to actual power plant stack gas. Phase II (1972-73) included a study of the acidulation, stripping, and regeneration systems. Phase III (1973-76) was for integrated operation of the various steps of the process. The Phase I and II work was covered in detail in a report titled "Ammonia Absorption - Ammonium Bisulfate Regeneration Process, Topical Report Phases I and II," which was issued by EPA in 1974 (report EPA-650/2-74-049A). This work is highlighted in the present report as background for Phase III.

The pilot-plant studies resulted in the development of data suitable for design and operation of large-scale units for removing over 90% of the $SO_2$ in flue gases by reaction with $NH_3$ and for acidulating and stripping the absorber effluent liquor to release the $SO_2$ for recovery in desired form. Actual pilot-plant study of the ammonium sulfate [$(NH_4)_2SO_4$] decomposition step was not made and the project was terminated when a cost study, based on developed and theoretical data, indicated that this regenerable process would not be economically competitive when compared with other leading flue gas desulfurization (FGD) systems. A technology problem remaining unsolved is the development of operating conditions that will prevent the presence of a plume in the flue gas.

## Phase I

The $NH_3$ process for removing $SO_2$ from stack gases was selected for study as a result of a series of conceptual design studies made by TVA for the National Air Pollution Control Administration (NAPCA), now EPA. Two of the studies covered the use of limestone as a sorbent for $SO_2$ in dry and wet processes respectively. The third study was concerned with the use of $NH_3$ as the absorbent. The limestone processes are throwaway processes and no byproduct is redeemed. The $NH_3$ process offered two attractive advantages. Sulfur (S), a valuable natural resource, captured in the ammoniacal liquors, is conserved. Secondly, the absorber product liquor could be further processed to a useful and salable form. The sale of the byproduct would help to offset, at least partially, the cost of operation.

Much work had already been done on $NH_3$ absorption of $SO_2$. The well-known work by Johnstone and coworkers at the University of Illinois during the period 1935-52 and by Chertkov and coworkers in Russia during the 1950's and 1960's covered the fundamental chemical reaction kinetics as well as certain regeneration schemes. Cominco, in Trail, B.C., and others elsewhere have installed commercial- or semicommercial-scale $NH_3$ absorption processes for $SO_2$ abatement. TVA in the 1950's piloted an $NH_3$ absorption process for $SO_2$ removal from coal-fired power plant flue gas. Even with the extensive effort of these workers, some areas of the $NH_3$ process as applied to power plant flue gas cleanup were not well defined. These areas included absorber design, degree of oxidation of sulfites in the absorber loop, effect of flyash on absorber operation, and corrosion. Consequently, the Phase I work had as its specific objectives the design, construction, and operation of a pilot plant to investigate, in depth, the variables involved in $NH_3$ absorption of $SO_2$.

The chemistry of $NH_3$ absorption of $SO_2$ is represented by the following equations:

$$NH_3 + H_2O + SO_2 \rightleftharpoons \underset{\text{ammonium bisulfite}}{NH_4HSO_3} \qquad \text{(ES-1)}$$

$$2NH_3 + H_2O + SO_2 \rightarrow \underset{\text{ammonium sulfite}}{(NH_4)_2SO_3} \qquad \text{(FS-2)}$$

In the pilot-plant absorption unit tested in Phase I, flue gas passed through dust collectors, a cooler, and then a three-stage absorber (both a sieve-tray and a marble-bed absorber were tested). Over 90% of the $SO_2$ was removed from the flue gas in repeated tests. Removal of $SO_2$ was not affected by the temperature of the inlet gas in the range tested, 200-300°F (93.3-148.9°C), or by the level of flyash (1-6 gr/scf) in the gas. No mechanical problems were encountered in handling the absorber effluent liquor at either the low or high flyash loading. Ammonia losses in the gas from the absorber were kept below the arbitrarily set limit of 50 ppm by maintaining the pH of the liquor on the top (third) stage at 6.1 or less. The heat capacities of the absorber inlet and exit gases were 0.260 and 0.269 Btu/(lb)(°F), respectively, which are in close agreement with the literature. The rate of oxidation of the absorbed $SO_2$ in the absorber liquor was not quantitatively determined; the degree of oxidation ranged from about 5 to 25% and averaged about 13%. The effect of $(NH_4)_2SO_4$ concentration on $SO_2$ removal efficiency was slight, about 1-3 percentage points. Emission of a dense plume was identified as a potential problem with the $NH_3$ absorption process.

## Phase II

During Phase II, further study was to be made of operation of the absorber with emphasis on preventing the appearance of a plume in the exhaust gas. Also, equipment and operating conditions were to be developed for the $SO_2$ recovery and the ammonium bisulfate ($NH_4HSO_4$) regeneration step of the ABS process. This process was chosen over other processes for recovery of $SO_2$ from ammoniacal absorber liquor which contains ammonium sulfite [$(NH_4)_2SO_3$] and ammonium bisulfite ($NH_4HSO_3$) because it was a cyclic, regenerative process that provided for recycling of $NH_3$ to the absorber and permitted recovery of $SO_2$ as elemental S or sulfuric acid ($H_2SO_4$). The other processes reviewed but not included in the present study were (1) the thermal stripping processes of Johnstone and of Chertkov, which required high energy input to remove the $SO_2$ (12 lb steam/lb recovered $SO_2$); (2) an autoclave process to produce elemental S and ammonium sulfate [$(NH_4)_2SO_4$]; the process was reported to be difficult to control and to be highly corrosive; (3) $H_2SO_4$ acidulation process that would preclude regeneration of $NH_3$ and would require marketing of large tonnages of $(NH_4)_2SO_4$.

The chemistry for the ABS process regeneration section is as follows:

Acidulation:

$$(NH_4)_2SO_3 + 2NH_4HSO_4 \rightarrow 2(NH_4)_2SO_4 + H_2O + SO_2\uparrow \quad (ES\text{-}3)$$

$$NH_4HSO_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4 + H_2O + SO_2\uparrow \quad (ES\text{-}4)$$

Decomposition:

$$(NH_4)_2SO_4 \xrightarrow{heat} NH_4HSO_4 + NH_3\uparrow \quad (ES\text{-}5)$$

The absorber product liquor, which contains $(NH_4)_2SO_3$ and $NH_4HSO_3$ is acidulated with "regenerated" $NH_4HSO_4$ to produce $(NH_4)_2SO_4$ solution and release $SO_2$ (eqs. ES-3 and -4). The $(NH_4)_2SO_4$ solution is evaporated and the resultant crystals are decomposed thermally (eq. ES-5) to release $NH_3$ for recycling to the absorber and to form $NH_4HSO_4$ for use in acidulating the absorber product liquor.

In the Phase II pilot plant, the flyash collector and the heat exchanger were omitted because, as was stated earlier, flyash loading and inlet-gas temperature did not affect $SO_2$ removal in the ranges tested. Also, the first stage of the three-stage marble bed absorber used in the Phase I work was replaced with a valve-tray element so that plume studies could be conducted with the absorber. The plume studies required that at times the bottom stage be deactivated. During deactivation, the hot (300°F) flue gas would have heated the marble bed and subjected the marbles to destruction by thermal shock, should the cold absorber liquor be pumped to the element or fall to the element from an upper stage.

Another change from planned study was acidulation of the absorber product liquor with $H_2SO_4$ instead of with $NH_4HSO_4$ because equipment for thermal decomposition of $(NH_4)_2SO_4$ was not available. This substitution was not expected to affect the test results. In the Phase II tests, acidulation of the absorber product liquor was essentially complete at acid ion to $NH_3$ ion ratios of slightly over 1.0 but much higher (up to 2.0) ratios were required to release and strip all the $SO_2$ from the acidulated solution. It was concluded that a new equipment design would improve $SO_2$ recovery so that no more than 0.5 g/l of S from $SO_2$ would be retained in the stripped solution with an acid ion to $NH_3$ ion ratio of near 1.0.

Crystalline $(NH_4)_2SO_4$ was produced by evaporating water from the solution of $(NH_4)_2SO_4$ in a tank at atmospheric pressure. However, crystal growth could not be controlled and separation with a centrifuge or a tub filter was inadequate. All filter media were blinded by a mudlike material believed to be a ferrous ammonium sulfate. Discussions with equipment vendors and $(NH_4)_2SO_4$ producers indicated that adequate crystal growth and separation could be obtained with commercially available evaporator-crystallizer equipment.

Considerable work was done in an effort to develop a method for controlling or eliminating the plume that had plagued all of the work on absorbing $SO_2$ in ammoniacal liquor. Several methods have been used by others, including wet-electrostatic precipitators and impaction-type collectors. These methods allow the fume to form in the absorber and, at added cost to the process, remove the solids from the gas stream. A private company, Air Products and Chemicals, Inc., proposed a different approach, on the assumption that the plume is $NH_4HSO_3$ formed in a vapor-phase reaction. They proposed to prevent $NH_4HSO_3$ fume formation in the absorber by controlling the conditions conducive to its formation, i.e., the concentration of $SO_2$, $NH_3$, and $H_2O$ in the vapor phase. This concept was tested in a joint EPA-TVA-Air Products pilot-plant program. Results were not consistently satisfactory. However, in a majority of the tests, the plume opacity was acceptably low (5% or less considered acceptable in the pilot plant; 20% or less required for a "commercial" stack), providing the following operating conditions were used:

1. A water wash ahead of the absorber.
2. Scrubbed gas reheated to the temperature necessary to dissipate the steam plume.
3. Absorber and all downstream ducts insulated.

Subsequent tests in Phase III showed that neither gas reheat to 200°F nor insulation contributed appreciably toward elimination of the plume.

### Phase III

The pilot plant used in the previous studies was modified to include a prewash section and a four-stage absorber. The prewash section (venturi) was added to adiabatically cool and saturate the flue gas before the gas entered the absorber. It was operated with a pressure drop of 10 in. of $H_2O$ and a liquid to gas (L/G) ratio of 20 gal/1000 $ft^3$ (approximately 55 gpm of recirculating wash liquor). Each of the absorber stages contained a valve-tray element (Koch FlexiTray). However, these elements, under some conditions, permitted liquor transfer from one stage to the next higher stage by mist carryover. Some liquor also fell down through the stages. True-stage separation was not achieved.

In continued studies directed toward elimination of the plume, tests were made of a TVA modification of the Air Products concept based on the premise that the salt portion of the fume that formed in the absorber is ammonium sulfite monohydrate [$(NH_4)_2SO_3 \cdot H_2O$]. Predictions of the fume formation were made from a thermodynamic equation derived from the equilibrium constant for the reaction:

$$2NH_3 + 2H_2O + SO_2 = \underset{\text{ammonium sulfite monohydrate}}{(NH_4)_2SO_3 \cdot H_2O} \qquad \text{(ES-6)}$$

If the product of the vapor pressures of $NH_3$, $H_2O$, and $SO_2$ above the liquor on the trays exceeds the solubility product for these constituents, gas phase precipitation of $(NH_4)_2SO_3 \cdot H_2O$ will occur, thus forming a fume. Tests of this concept indicated it to be valid and accurate but with limitations. For example, there is no way to compensate for any possible effect that the $SO_3$ and chlorides in the flue gas may have on the predictions.

The absorber test program of the TVA concept was designed to control the $SO_2$ vapor pressure above the trays by manipulating the pH and concentration of the absorber liquor. The desired product liquor concentration was 10-12 mols of sulfite $NH_3$/100 mols of $H_2O$ ($C_A$ = 10-12). The desired mol ratio of $SO_2$ to active $NH_3$ ($S/C_A$) was 0.78 for the first-stage liquor and 0.72 for the second stage. Consistent plumeless operation (pilot-plant stack opacity less than 5%) was not achieved, partly because of the inability to control the liquor concentration in the valve-tray absorber. Modifications to the absorber stages increased absorber liquor control but still did not ensure consistent plumeless operation.

An inline-indirect steam-heated reheater dissipated the $H_2O$ vapor in the scrubbed flue gas but did not significantly reduce the opacity of the plume. The scrubbed flue gas was reheated to 175°F in most tests.

A bench-scale study was made to investigate fume formation. Air, flue gas, or bottled gas (950 ppm $SO_2$) was pulled through a sample train, and $H_2O$, ammonium hydroxide ($NH_4OH$), hydrogen peroxide ($H_2O_2$), fuming $H_2SO_4$ (20% oleum), 20% hydrochloric acid (HCl), and 90% isopropyl alcohol were used as scrubbing media. An absolute filter was placed at different positions within the sample train during each test to try to capture the fuming agent. The absolute filter was able to remove it once the fume had formed. When the filter was placed in the flue gas stream before the sample train, the filter prevented the formation of the fume. The tests indicated that chlorides and sulfates in the flue gas are contributors to fume formation. However, other materials, such as flyash, which could serve as sites on which fume particles grow, and organics also may be involved. Further bench-scale work is needed to identify the cause of fume formation.

In the tests of recovering $SO_2$ from the absorber product liquor, 93% $H_2SO_4$ and heated ammoniacal liquor were fed simultaneously and continuously to a mixing pot acidulator. The acid ion to $NH_3$ ion [from $(NH_4)_2SO_3$ and $NH_4HSO_3$] mol ratio was 1.05. All of the ammonium sulfite and bisulfite in the liquor was acidulated. The acidulated material overflowed into a stripper which consisted of a 4-in.-diameter plastic pipe having three 10-ft packed sections (Tellerette packing). Almost all (99.9%) of the $SO_2$ evolved was removed in the stripper using 30 ft of packing and 5 ft³/min [10 ft³/(min)(gals of acidulated material)] of air as the stripping gas. The combined gas streams from the acidulator-stripper contained about 63% $SO_2$ which is more than adequate for a feed gas stream to an $H_2SO_4$ plant.

The acidulated and stripped liquor [$(NH_4)_2SO_4$ solution] was concentrated in a single-effect evaporator-crystallizer, operated at 175°F and 22 in. mercury (Hg) vacuum, to obtain a slurry of crystalline $(NH_4)_2SO_4$. Both a vacuum-belt filter and a screen-bowl centrifuge gave good separation of crystals from the slurry, which contained 10-25% solids. The moisture content of the crystals recovered from the slurry was about 5%.

An electrical, thermal $(NH_4)_2SO_4$ decomposer was designed with the assistance of a consultant and private industry. However, as stated earlier, the development program was canceled because of economic considerations, and the decomposer was not built. Therefore, the complete ABS process was not demonstrated as a cyclic process.

Corrosion test specimens of nine alloys, three plastics, and three rubbers were exposed at two locations in the pilot plant. One spool of specimens was immersed in the prewash sump and the other in the gas duct downstream from the chevron-type mist eliminator and ahead of the absorber. The corrosion rates for the alloys ranged from less than 1 mil/yr for Inconel 625 in both locations to 1126 mils for Incoloy 800 in the sump liquor. The three rubbers and two plastics tested in the treated flue gas duct showed little deterioration.

## ECONOMIC EVALUATION

Estimates were made to permit comparison of the cost of the ammonia absorption - ammonium bisulfate (ABS) regeneration process as originally envisioned with costs of several other FGD processes. The estimates were based on 1975 costs and available technology. Each process was designed to desulfurize the flue gas from a 500-MW, new, coal-fired power plant burning coal with 3.5% S (dry basis). The processes considered in this study and the results are presented in the following tabulation:

## Summary Of Costs Of Flue Gas Desulfurization Processes[a]

| | | Total capital investment, MM, $ | Net unit revenue requirement, mills/kWh[b] |
|---|---|---|---|
| 1. | Ammonia absorption - ammonium bisulfate regeneration - sulfuric acid production[c] | 42.1 | 3.42 |
| 2. | Ammonia absorption - scrubbing liquors saturated with ammonium sulfate - ammonium sulfate production | 31.5 | 2.87 |
| 3. | Limestone slurry absorption - ponding of sludge | 30.7 | 2.97 |
| 4. | Magnesia slurry absorption - sulfuric acid production[c] | 32.3 | 2.48 |
| 5. | Sodium sulfite absorption - sulfuric acid production[c] | 37.1 | 3.19 |

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[a] Basis:
500-MW new coal-fired power unit, 90% $SO_2$ removal.
Coal burned, 1,312,500 tons/yr, 3.5% S (dry basis), 9,000 Btu/kWh.
Stack gas reheat to 175°F by indirect steam reheat, entrained water 0.5% by wt (wet basis).
Power unit on-stream time, 7000 hr/yr.
Midwest plant location, 1975 revenue requirements.
Investment and revenue requirements for disposal of flyash excluded.
Remaining life of power plant, 30 yr.

[b] Includes revenue from sale of byproduct: $30/ton 100% sulfuric acid; $44/ton ammonium sulfate; $24/ton sodium sulfate.

[c] Regeneration process.

Of the five processes, the ABS regeneration process with production of sulfuric acid (No. 1) required the highest total capital investment, $42.1 million, and the highest unit revenue, 3.42 mills/kWh. Process 2, a noncyclic adaptation of the ABS process with production of ammonium sulfate, had a total capital investment requirement of $31.5 million and a unit revenue requirement of 2.87 mills/kWh. Both of these ammonia absorption processes were assumed to be operated without a stack plume by control of absorber conditions. Should this not be found feasible, wet-electrostatic precipitators could be used with increases in costs. These increases would be about 14% in total capital requirement and 4% in unit revenue requirement for the ABS process and 20% in capital and 5% in unit revenue requirement for the noncyclic ammonia process.

Process 3, removal of $SO_2$ by absorption in limestone slurry and disposal of the sulfur-containing sludge in ponds, had a total capital requirement of $30.7 million and a revenue requirement of 2.97 mills/kWh. If sludge fixation is practiced, the unit revenue requirement will increase by about 17%.

The magnesia slurry absorption process with regeneration of magnesia and production of sulfuric acid had a total capital requirement of $32.3 million and a unit revenue requirement of 2.88 mills/kWh.

The sodium sulfite absorption process (regeneration) with sulfuric acid production required $37.1 million in total capital and the unit revenue requirement was 3.19 mills/kWh.

A limited study, sponsored by EPA, was made of the economics of using $(NH_4)_2SO_4$ from an ammonia scrubbing FGD process as a replacement for anhydrous $NH_3$ for direct application of nitrogen to the soil. It was assumed that the ammonia planned for direct application would first be routed to the power plant, then used for absorbing $SO_2$ from the flue gas, and recovered as $(NH_4)_2SO_4$, which then would be transported and applied to the soil as a replacement for anhydrous $NH_3$.

Two power plant locations in the Midwest were used in the study, one in an area of high-density agricultural $NH_3$ consumption and one in an area of relatively low consumption.

The results of this study indicated that the sum of the costs of handling, transporting, storing, and applying a ton of $NH_3$ to the soil as $(NH_4)_2SO_4$ may be about $26 less than that for $NH_3$ as anhydrous $NH_3$ in the high-use area and about $8 less in the low-use area. The cost of FGD is not included.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

1. The absorption efficiency (90% and higher) can be reliably predicted for given operating parameters.

2. Ammonium sulfate levels in the absorber loop have only slight influence on $SO_2$ absorption.

3. Flyash has a negligible effect on $SO_2$ removal.

4. Temperature of the inlet flue gas has little effect on $SO_2$ removal in the range covered by the study (180 to 300°F).

5. Corrosion was not a problem in the absorption loop when using stainless steels and certain nonmetals.

6. Corrosion in the regeneration loop requires use of low-carbon stainless steel and plastics.

7. Effective and consistent plume control was not achieved by methods and equipment tested in the pilot plant.

8. An inline-indirect steam-heated reheater dissipated the $H_2O$ vapor in the scrubber flue gas but did not significantly reduce the opacity of the $NH_3$-S compound plume.

9. Bench-scale studies identified chloride and $SO_3$ (both found in the inlet flue gas) as fuming agents.

10. Predictions of the formation of the fume, presumably $(NH_4)_2SO_3 \cdot H_2O$, can be made from a thermodynamic equation derived from the equilibrium constant for the reaction:

$$2NH_3 + 2H_2O + SO_2 \rightleftharpoons (NH_4)_2SO_3 \cdot H_2O \qquad \text{(ES-7)}$$

    This study shows that the fume prediction equations must be satisfied as a necessary but not limiting condition for fumeless operation, for instance, chlorides and $SO_3$ are not considered in the equation.

11. Complete acidulation of the absorber product liquor was accomplished using $H_2SO_4$.

12. 99.9% of the $SO_2$ in the $(NH_4)_2SO_3$ and $NH_4HSO_3$ to the acidulator-stripper was recovered as $SO_2$.

13. The combined off-gas stream from the acidulator and stripper was approximately 60% $SO_2$ which is more than adequate for a feed gas stream to a sulfuric acid plant.

14. The evaporator-crystallizer produces an $(NH_4)_2SO_4$ slurry suitable for crystal separation.

15. Standard $(NH_4)_2SO_4$ separation techniques appear to be acceptable for removing crystalline $(NH_4)_2SO_4$ from the evaporator-crystallizer slurry.

16. A comparative economics study of the ABS process and other more advanced regenerable and nonregenerable processes (500-MW units) showed that the ABS process was not competitive with other FGD processes. An $NH_3$ absorption-$(NH_4)_2SO_4$ production nonregenerable process is suggested as having economic potential.

## Recommendations

1. Developmental work on the ABS process should cease because of unfavorable economics, chiefly associated with the high cost of decomposing $(NH_4)_2SO_4$ for regeneration of $NH_3$ and production of molten $NH_4HSO_4$. No breakthroughs are foreseen that would make it economically competitive with other regenerative processes.

2. The emphasis of any further $NH_3$ absorption pilot-plant work should be directed toward a nonregenerable process so as to eliminate the costly decomposition step. The $NH_3$ absorption system can produce $(NH_4)_2SO_4$, a N source in the formulation of some fertilizers. Preliminary results of a market study show that $(NH_4)_2SO_4$ produced during $SO_2$ absorption can be sold as a fertilizer at a price high enough to recover the cost of the $NH_3$. The study also shows that the $NH_3$ absorption process with production of $(NH_4)_2SO_4$ is at least as attractive, economically, as the limestone slurry process with simple sludge throwaway (2.87 and 2.97 mills/kWh respectively). Even with a mechanical or electrical particulate collector added to the system, the ABS process remains competitive.

# AMMONIA ABSORPTION/AMMONIUM BISULFATE REGENERATION PILOT PLANT FOR FLUE GAS DESULFURIZATION

## INTRODUCTION

A large portion of the pollution of our atmosphere is the 26-28 million tons of sulfur oxides exhausted annually by industry. Of this total, about 17.5 million tons originate at coal-fired power utilities. The need to decrease these sulfur oxide emissions has long been recognized. Methods for removing them from the gases and for recovering the sulfur in a useful form have been studied by many.

The Tennessee Valley Authority (TVA) has made a number of design and cost studies over the past years for the Environmental Protection Agency (EPA), formerly the National Air Pollution Control Administration (NAPCA), on methods for removing sulfur dioxide from stack gases. Two of these studies(1, 2) covered the use of limestone as an absorbent, in dry or wet processes, respectively. In both cases, the sulfur dioxide removed from the gas is discarded as calcium sulfate or sulfite. A third study(3) was concerned with the use of ammonia as the absorbent, in nonregenerative processes that recover a useful product that can be sold to partially offset the cost of the operation. With a view toward further developing the removal of $SO_2$ by scrubbing with ammonia, NAPCA contracted with TVA, in 1968, for an in-depth pilot plant study to be made on actual power plant flue gases. Also, it was envisioned that the work might eventually expand to developing a cyclic, regenerable process whereby the $SO_2$ would be recovered as sulfuric acid or elemental sulfur and the ammonia would be recycled to the absorption section.

A review of the literature revealed that $SO_2$ removal from gas streams by absorption in aqueous ammonia had been studied as far back as 1883 when a British patent was issued to Ramsey(4). In these early studies, ammonium sulfate $(NH_4)_2SO_4$ was the desired product. Around 1936 the Consolidated Mining and Smelting Company(5) (now Cominco, Ltd.) installed a commercial ammonia-$SO_2$ absorption unit for removal of sulfur oxides from waste smelter gases. Products from the unit were $(NH_4)_2SO_4$ and $SO_2$.

About the same time Cominco was developing a process, Johnstone and his coworkers at the University of Illinois were developing basic data for the ammonia system. Five major papers were published by Johnstone between 1935 and 1952 dealing with absorption of $SO_2$ by ammoniacal solutions and desorption from the absorber effluent(6-10). Measurements of vapor pressures in the system were made, and methods for regenerating the absorbing solution and recovery of byproducts were studied.

In 1953, TVA piloted an ammonia absorption process for removal of $SO_2$ from coal-fired power plant flue gases(11). TVA's objective was to recover the $SO_2$ as elemental sulfur. The process was abandoned when an anticipated sulfur market did not materialize. Considerable data have been gathered by Chertkov and his coworkers at NIIOGAZ (State Research Institute of Industrial and Sanitary Gas Cleaning) in Russia. This work began in the late 1950's and resulted in over 40 papers being published on sulfur oxide recovery, mostly involving ammonia absorption. All phases of the subject have been reported--basic chemical data, mass transfer in absorbers, the autoclave process, and several regeneration schemes. A large portion of the experimental work was done on a pilot scale. Plans are underway for equipping a 240-MW boiler with an ammonia absorption and thermal-stripping unit. In Japan, the Showa Denko Company has operated an ammonia absorption test unit (25 MW) on flue gases from an oil-burning boiler. Ammonium sulfate was the end product(12). In 1967 Ugine Kuhlman, Weiritam, and Electricite de France combined to construct and operate a 25-MW ammonia absorption unit at an EDF power plant near Paris(13).

Even with the extensive effort of these early workers, some areas of the ammonia process as applied to power plant flue gas cleanup were not well defined. These areas include: absorber design including multistaging to obtain optimum results, degree of oxidation of sulfites in the absorber loop, effect of flyash on scrubber operation, absorber product regeneration, and corrosion.

The current pilot-plant work was done in three phases, during the period 1969-76, at TVA's Colbert power plant in northwest Alabama. An aerial view of the Colbert plant is shown in Figure 1. The first two phases of this project, which were concerned with ammonia absorption of $SO_2$ and regeneration of ammonium bisulfate, were described in detail in Topical Report EPA-650/2-74-049-a, June 1974(14), and are reviewed herein for orientation purposes. The third, and last, phase, which ended in mid-1976, is described here in detail. This phase was designed for in-depth studies of problem areas that remained unsolved in the earlier work and for integrated operation of the pilot-plant components. However, all of the study and design objectives were not completed because a cost study, based on developed information, indicated unfavorable economics as compared to other flue gas desulfurization processes. The major unsolved technical problem was inability to prevent formation of a white plume in the exhaust gas from the $SO_2$ absorber

Figure 1. TVA Colbert power plant--site of EPA/TVA pilot-plant studies on removal of $SO_2$ from stack gas.

## PHASE I

The objective of the Phase I study was to construct a pilot-plant unit for removing $SO_2$ from actual coal-fired power plant flue gases and to operate it to determine the factors that influence the absorption of $SO_2$ in aqueous ammonia. The design of the pilot plant was based both on data from the literature and the mechanical requirements determined to be necessary for study of some of the parameters, such as corrosion and effect of flyash on $SO_2$ recovery. The pilot plant had a capacity of about 4,000 ft³ of flue gas per minute at 300°F, which is about that normally resulting from the production of 1.25 MW of electricity in a coal-fired power plant.

The chemistry of the process for $SO_2$ absorption in an aqueous ammonia system is represented by the following equations:

$$NH_3 + H_2O \rightarrow \underset{\text{ammonium hydroxide}}{NH_4OH} \qquad (1)$$

$$NH_4OH + SO_2 \rightarrow \underset{\text{ammonium bisulfite}}{NH_4HSO_3} \qquad (2)$$

$$NH_4HSO_3 + NH_3 \rightarrow \underset{\text{ammonium sulfite}}{(NH_4)_2SO_3} \qquad (3)$$

$$(NH_4)_2SO_3 + SO_2 + H_2O \rightarrow \underset{\text{ammonium bisulfite}}{2NH_4HSO_3} \qquad (4)$$

The primary reactions during steady-state absorber operation are represented by equations 3 and 4, the formation of $(NH_4)_2SO_3$ and $NH_4HSO_3$.

Figure 2 is a flowsheet of the ammonia absorption process as used in the Phase I studies. The pilot-plant equipment included flyash collectors to permit study of the effect of flyash on ammonia ($NH_3$) absorption; a gas cooler for use in studying the effect of flue gas temperature; and a three-stage scrubbing system, including recirculation tanks.

The Phase I pilot plant was operated about 2,000 hr during 1970-72. These studies showed that the ammonia process was

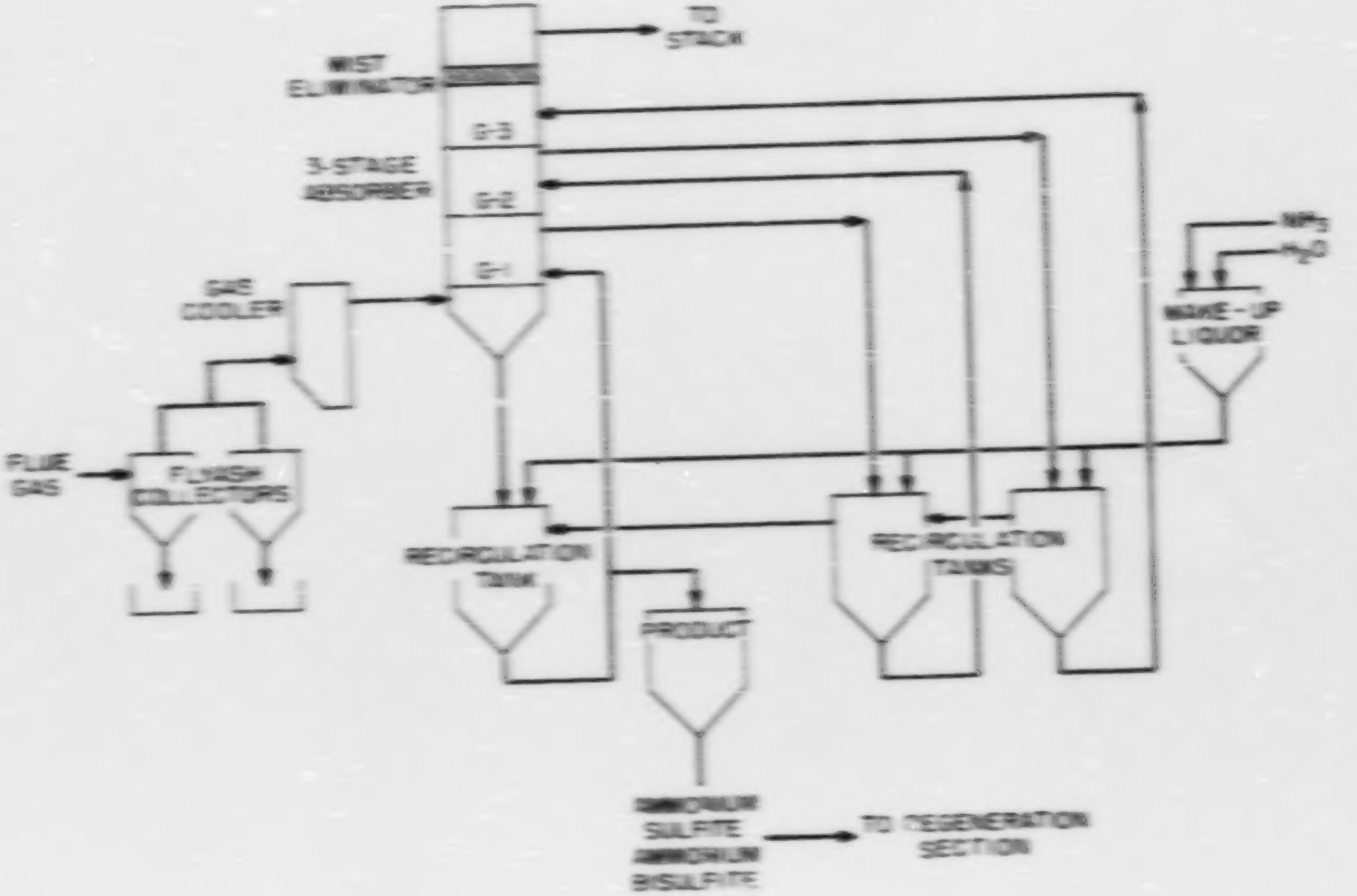

TO STACK
MIST ELIMINATOR
3-STAGE ABSORBER
G-3
G-2
G-1
GAS COOLER
FLUE GAS
FLYASH COLLECTORS
RECIRCULATION TANK
PRODUCT
RECIRCULATION TANKS
NH3
H2O
MAKE-UP LIQUOR
AMMONIUM SULFITE
AMMONIUM BISULFITE
TO REGENERATION SECTION

Figure 2. Phase I—Absorption of $SO_2$ by ammoniacal liquors.

effective in removing $SO_2$ from power plant flue gas; removal
efficiencies of 90% and greater were routinely obtained in the
three-stage absorber. The temperature of the inlet flue gas had
little or no effect on $SO_2$ removal over the range (200 to 300°F)
tested. It had been expected that a temperature increase would
decrease $SO_2$ removal efficiency; the data from the tests show an
increase of about three precentage points in $SO_2$ removal
efficiency as temperature was increased from 200 to 300°F. This
increase was attributed to the increase in the quantity of makeup
water added to the top stage to replace water removed by the gas
at the higher temperature

The level of flyash (1-3 gr/scf) in the inlet flue gas had no
effect on $SO_2$ removal nor did it cause any mechanical handling
problems.

Ammonia losses in the gas from the absorber were kept within
the arbitrarily set limit of 50 ppm by maintaining the pH of the
liquor on the top (third) stage at 6.1 or less.

The effect of sulfate on $SO_2$ removal efficiency was found to
be slight.

Heat transfer data obtained during the Phase I work indicated
the heat [illegible]ties of the inlet and absorber exit gases were
0.260 and 0.[illegible] Btu/(lb)(°F) respectively. These values compared
closely with literature values for similar gases. The overall
heat transfer coefficient for a tube-and-shell heat exchanger
with flue gas on the shell side was determined to be 2.7
Btu/(hr)(ft²)(°F) after several months' operating time. The
value is much lower than the manufacturer's stated Uo of 11.3
Btu/(hr)(ft²)(°F) for new conditions. The difference is at least
partially explained by fouling of the tubes; during operation,
the tube surfaces were cleaned periodically with steam-operated
soot blowers and, during shutdowns, they were cleaned with high-
velocity water lances.

The rate of oxidation of the absorbed $SO_2$ in the absorber
liquor was not quantitatively determined. The degree of
oxidation ranged from 5 to 25% with an average of about 13%.

Corrosion was not a problem where resistant materials (SS and
nonmetals) were used.

Emission of a dense plume was identified as a potential
problem with the ammonia absorption process.

## PHASE II

Even with the plume problem, the favorable results from the Phase I work led EPA and TVA to continue and extend the work as Phase II. The new program was to include a study of a process for recovering the $SO_2$ in useful form in order to conserve a valuable resource. The $SO_2$ recovery process also was to include recovery of the ammonia for recycling to the $SO_2$ absorption system.

Several processes were available which produced $SO_2$ (or sulfur) from ammoniacal solution. Johnstone's and Chertkov's studies included recovery of $SO_2$ from the ammoniacal solutions. The Ugine Kuhlmann, Weritam, and Electricite de France pilot-plant study also included an $SO_2$ recovery system; these systems used the thermal-stripping method for $SO_2$ release. The Cominco process uses an acid ion (from sulfuric acid) to release the absorbed $SO_2$ from the ammoniacal liquor(15). The released $SO_2$ is sent to a sulfuric acid plant. A portion of the acid is returned to the acidulation step and the surplus is disposed of either directly or as ammonium sulfate in their fertilizer facilities. Also, a process has been patented that produces elemental sulfur directly(16). The absorber effluent is auto-oxidized in an autoclave under elevated pressure and temperature to produce elemental sulfur and ammonium sulfate. TVA briefly studied the process in the 1950's(17).

Each of the foregoing processes has certain drawbacks that removed them from consideration for the EPA-TVA study. Thermal stripping, for instance, is a high energy-consuming process (17 lb of steam per lb of recovered $SO_2$) and is also plagued by a side reaction which produces thiosulfates. In the autoclave process, corrosion is severe and process control is difficult. Moreover, it was decided that the process selected should be truly cyclic, that is, the ammonia was to be recycled to the $SO_2$-absorption step and only the recovered sulfur was to leave the system, whereas each of the above systems produce byproduct ammonium sulfate.

The decision then was made by EPA and TVA that a process similar to that proposed by Hixon and Miller in 1944(18) be considered. In this process [later modified by Jordan and Newcombe (19)], the $(NH_4)_2SO_3$ and $NH_4HSO_3$ in the absorber product liquor are aciduiated with ammonium bisulfate ($NH_4HSO_4$), with the formation of ammonium sulfate [$(NH_4)_2SO_4$] and $SO_2$ in solution. The $SO_2$ is stripped from the solution with air. The $(NH_4)_2SO_4$ is crystallised and removed from the solution and then is thermally decomposed to $NH_3$ for recycle to the absorber and to $NH_4HSO_4$ for recycle to the acidulation step. The reactions for this sequence are:

Acidulation:

$$\underset{\text{ammonium sulfite}}{(NH_4)_2SO_3} + \underset{\text{ammonium bisulfate}}{2NH_4HSO_4} \rightarrow \underset{\text{ammonium sulfate}}{2(NH_4)_2SO_4} + H_2O + SO_2 \tag{5}$$

$$\underset{\text{ammonium bisulfite}}{NH_4HSO_3} + \underset{\text{ammonium bisulfate}}{NH_4HSO_4} \rightarrow \underset{\text{ammonium sulfate}}{(NH_4)_2SO_4} + H_2O + SO_2 \tag{6}$$

Decomposition:

$$\underset{\text{ammonium sulfate}}{(NH_4)_2SO_4} \xrightarrow{\text{heat}} \underset{\text{ammonium bisulfate}}{NH_4HSO_4} + NH_3 \tag{7}$$

In this work, acidulating and stripping the absorber product liquor was to be studied. Since an ammonium sulfate decomposer was not available, sulfuric acid ($H_2SO_4$) was used as the acid source. Use of $H_2SO_4$ instead of $NH_4HSO_4$ was justified because, in solution, a mixture of $H_2SO_4$ and $(NH_4)_2SO_4$ will differ from an $(NH_4)HSO_4$ solution only by the sulfate to ammonia ratio.

Flow diagrams of the absorption and regeneration sections of the pilot plant used in Phase II are shown in Figures 3 and 4. The first stage of the three-stage marble bed absorber used in the Phase I work was replaced with a valve-tray element so that plume studies could be conducted with the absorber. The plume studies required that at times, the bottom stage be deactivated. The marble bed would be heated when deactivated to near the inlet gas temperature (300°F) and the marbles would be subject to destruction by thermal shock should liquor inadvertently be pumped to the element or fall on it from an upper stage while the element is hot.

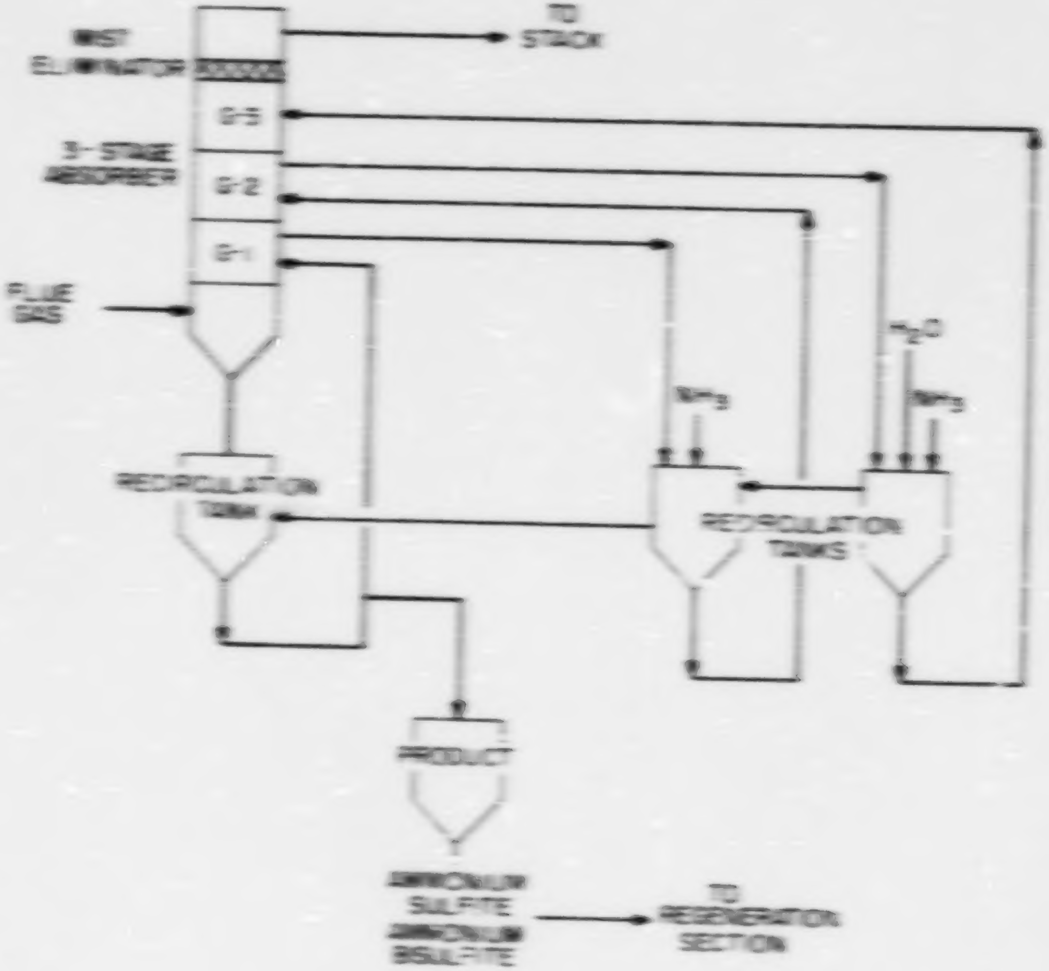

TO STACK
MIST ELIMINATOR
G-3
3-STAGE ABSORBER
G-2
G-1
FLUE GAS
RECIRCULATION TANK
$NH_3$
$H_2O$
$NH_3$
RECIRCULATION TANKS
PRODUCT
AMMONIUM SULFITE
AMMONIUM BISULFITE
TO REGENERATION SECTION

Figure 3. Phase II—Absorption of $SO_2$ by ammoniacal liquors

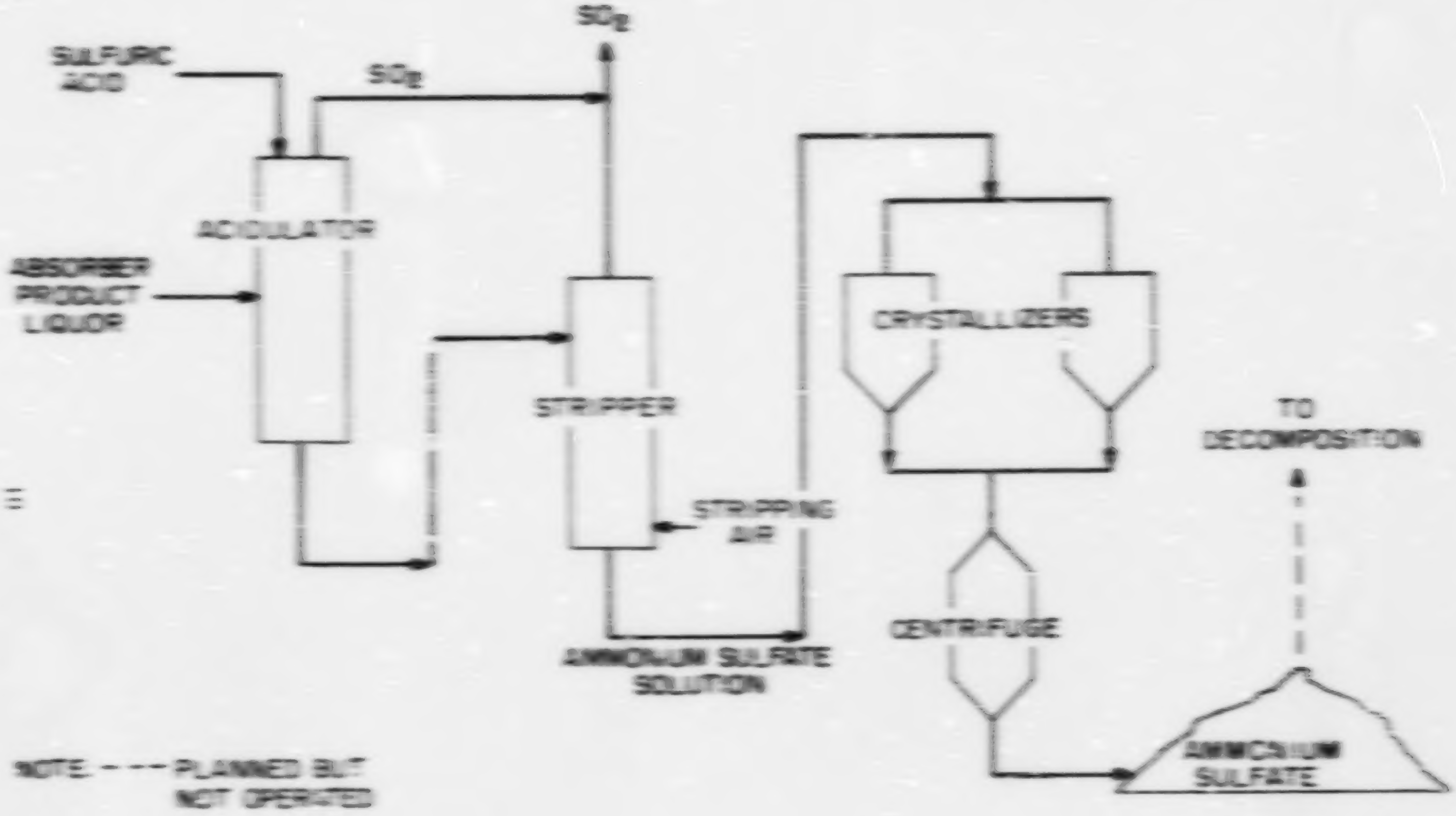

SULFURIC ACID
SO2
SO2
ACIDULATOR
ABSORBER PRODUCT LIQUOR
STRIPPER
STRIPPING AIR
AMMONIUM SULFATE SOLUTION
CRYSTALLIZERS
CENTRIFUGE
TO DECOMPOSITION
AMMONIUM SULFATE
NOTE: - - - PLANNED BUT NOT OPERATED

Figure 4. Phase II–Regeneration section–$SO_2$ recovery.

The regeneration section included $SO_2$ recovery equipment consisting of an acidulator and stripper and a tank with a steam-coil system to evaporate the resultant ammonium sulfate solution to produce crystals at atmospheric pressure.

Results of the study showed that acidulation of the $(NH_4)_2SO_3$ and $NH_4HSO_3$ was essentially complete at acid ion to ammonia ion mol ratios slightly in excess of 1.0 but that much higher ratios were required to release and strip all the $SO_2$ from the acidulated solution. It was concluded that a new equipment design would improve the $SO_2$ recovery so that no more than 0.5 g/l of sulfur from $SO_2$ would be retained in the stripped solution with acid ion to ammonia ion ratios of near 1.0. This was proven later in Phase III work.

Of major interest in the Phase II work was the study to develop a method to control or eliminate the plume that has plagued all of the ammonia absorption work. Several methods have been used in attempts to remove the plume. The Russians(20) have used wet electrostatic precipitators downstream of the absorber. U.S. paper companies have used the impactor-type (Monsanto Brink system) collector. Equipment vendors have proposed use of combination scrubber-precipitators to collect the plume as well as to absorb $SO_2$.

All the above concepts for control allow the plume to form, then, at added cost, remove it from the gas stream. TVA and a private company, Air Products and Chemicals, Inc., proposed trying to prevent plume formation rather than treating the plume after it formed. In the Air Products concept(21), the plume is assumed to be solid $NH_4HSO_3$ formed in a vapor phase reaction. Air Products proposed that formation of this solid (fume)[1] be prevented by controlling the conditions conducive to its formation, i.e., the concentrations of $SO_2$, $NH_3$, and water in the vapor phase. Ammonia also reacts with chlorides and $SO_3$ to form solid phases as evidenced by chemical analysis of solids removed from the gas stream and by results of the bench-scale studies discussed later. The prewash section was operated under conditions that minimized the quantity of these materials reaching the ammonia absorption step.

Tests were made to examine the Air Products concept. In these tests, only one absorber stage was used; therefore, $SO_2$

---

[1] For the sake of clarity, _fume_ will refer to the solid gas phase reaction products inside the absorber and _plume_ will refer to the reaction products plus ash and water vapor exiting the pilot plant stack.

removal efficiency was low, as expected. In most but not all tests, the plume opacity met the 5% or less requirement set for the pilot-plant stack (industrial stack requirement is 20% or less; see discussion later) providing the following operating conditions were used:

1. A water wash was present ahead of the absorber.
2. The scrubbed gas was reheated to the temperature necessary to dissipate the steam plume.
3. The absorber and all downstream ducts were insulated.

## PHASE III

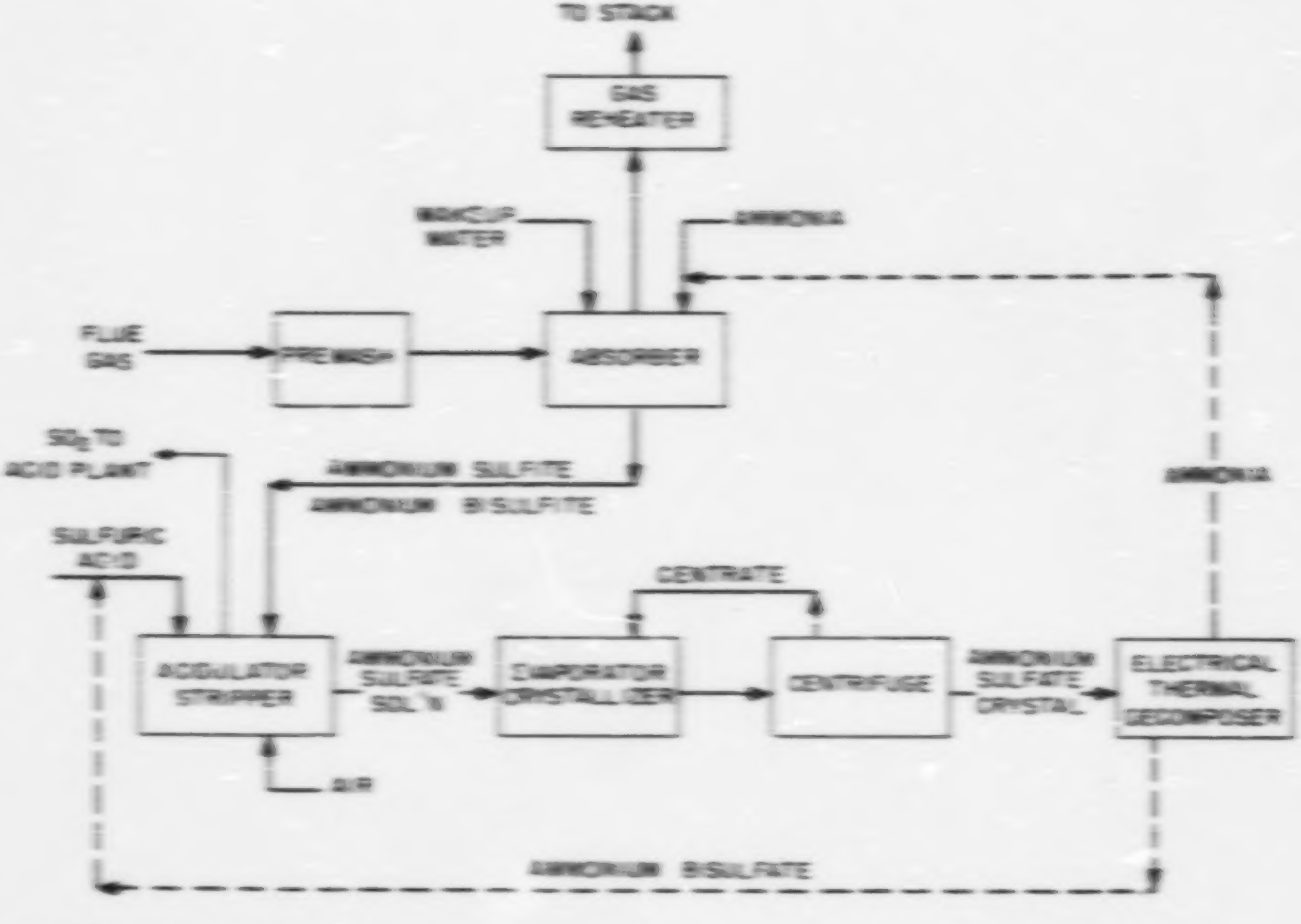
The original intent of the Phase III study was to:

1. Overcome the absorber plume problem.
2. Develop acidulation and stripping techniques so that no more than 0.5 g/l of absorbed $SO_2$ remained in the stripper effluent.
3. Demonstrate removal of ammonium sulfate crystals from regeneration section.
4. Develop and test an ammonium sulfate decomposer.
5. Demonstrate the technical feasibility of the complete regenerable system.

In addition, an economic comparison of the ABS process with other regenerable processes was to be made with updated cost and technical data, including data generated during development of the decomposer. As stated earlier, the economic comparison was unfavorable for the ABS process, and a decision was made to discontinue the pilot-plant study. Therefore, the ammonium sulfate decomposer was not constructed and the complete process was not demonstrated. Also, a question still remained on how to eliminate the plume in a feasible way.

### DESCRIPTION OF PILOT PLANT

The pilot plant used in the previous work was modified for the Phase III work. A simplified flowsheet is shown in Figure 5. A stack gas prewash section was installed in the gas line to the scrubber because the Phase II work had indicated possible control of fume formation if the gas were cooled and humidified before it came in contact with ammoniacal liquor in the absorber. The three-stage absorber was replaced with a four-stage valve-tray absorber; the fourth, or last stage, was used for scrubbing the gas with water to remove entrained absorber-liquor before the gas passed through the mist eliminator (Heil Process Equipment Corporation). The marble beds were replaced with valve trays


TO STACK
GAS REHEATER
MAKEUP WATER
AMMONIA
FLUE GAS
PREWASH
ABSORBER
$SO_2$ TO ACID PLANT
AMMONIUM SULFITE
AMMONIUM BISULFITE
AMMONIA
SULFURIC ACID
CENTRATE
ACIDULATOR STRIPPER
AMMONIUM SULFATE SOL'N
EVAPORATOR CRYSTALLIZER
CENTRIFUGE
AMMONIUM SULFATE CRYSTAL
ELECTRICAL THERMAL DECOMPOSER
AIR
AMMONIUM BISULFATE

NOTE: ---- PLANNED BUT NOT OPERATED

Figure 5. Ammonia absorption–ammonium bisulfate regeneration process for removing $SO_2$ from power plant stack gas.

because liquor would suddenly and uncontrollably fall from a marble bed to the next lower stage, with loss of control of absorber-liquor concentration at each stage. Other modifications included replacing the Phase II acidulation and $SO_2$ stripping equipment with a new acidulator and large stripper, and replacing the atmospheric ammonium sulfate evaporator-crystallizer with a vacuum-operated system to improve crystal growth and to avoid the excessive corrosion encountered at the elevated temperature required for atmospheric evaporation.

## Absorption Section

Figure 6 is a detailed flowsheet of the absorption section.

### Prewash--

Flue gas to the prewash unit was withdrawn from one of the Colbert boiler ducts (either unit 3, 4, or 5) downstream of the electrostatic precipitator. (Provisions were made for obtaining flue gas upstream of the precipitator; however, most of the Phase III work was done with gas taken from downstream of the precipitators.) The flue gas (300°F) typically contained about 2,800 ppm $SO_2$, 10-45 ppm chloride as HCl, and about 0.1 gr flyash/scf. The gas flowed through two forced-draft constant-speed blowers and entered the top of the prewash unit, a schematic of which is shown in Figure 7. The gas then turned downward and flowed vertically through a 1- by 1-ft interior duct that had near the duct outlet a venturi-type rod element similar to Environeering's Ventri-rod element. The rods were made from 3/4-in. chlorinated polyvinyl chloride (CPVC) plastic pipe, and the number of rods could be varied to increase or decrease the pressure drop across the element. Liquor was recirculated to the rod element at an L/G of about 10 gal/1000 $ft^3$ of gas to cool and humidify the gas. Makeup water to replace that lost to humidification entered the system through a spray nozzle in the inlet section. The spray nozzle was set so that the water struck the walls at the top of the fiberglass reinforced plastic (FRP) duct to protect the FRP from the hot gas. The gas leaving the rod element impinged on the surface of liquor in the prewash sump, reversed direction and flowed upward through the annular space between the inlet duct and prewash housing. Near the top of the prewash unit, the gas turned horizontally and passed through a Heil chevron mist eliminator and entered the bottom section of the absorber tower.

The prewash housing was constructed of FRP (Atlac 382) coated with an epoxy resin paint for protection against severe corrosion. (A temporarily installed humidification section constructed of 316L SS corroded at excessive rates--see Appendix C, Corrosion.) The inlet or transition section to the FRP unit

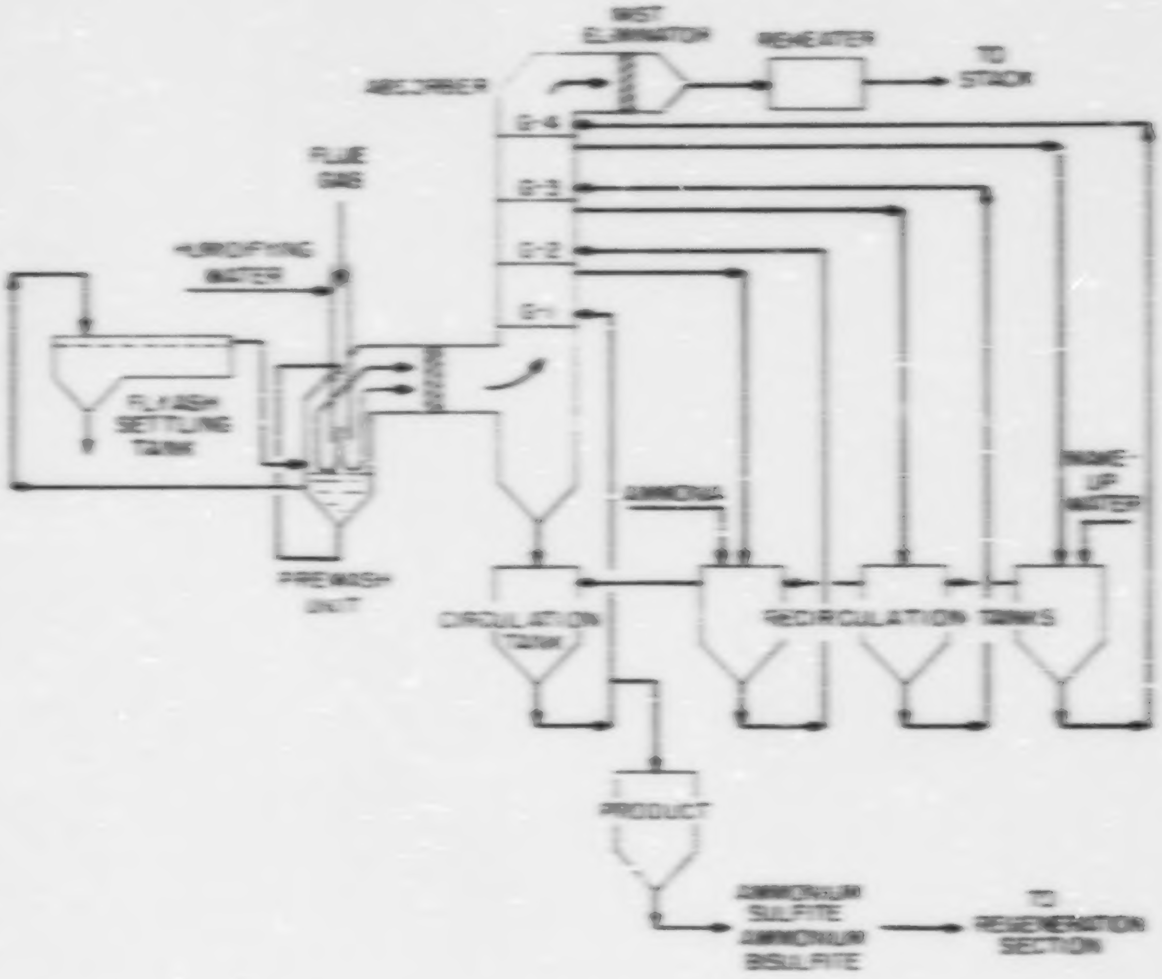

MIST ELIMINATOR
REHEATER
TO STACK
ABSORBER
G-4
G-3
G-2
G-1
FLUE GAS
HUMIDIFYING WATER
FLYASH SETTLING TANK
PREWASH UNIT
AMMONIA
MAKE-UP WATER
CIRCULATION TANK
RECIRCULATION TANKS
PRODUCT
AMMONIUM SULFITE AMMONIUM BISULFITE
TO REGENERATION SECTION

Figure 6. Phase III – Absorption of $SO_2$ by ammoniacal liquors.

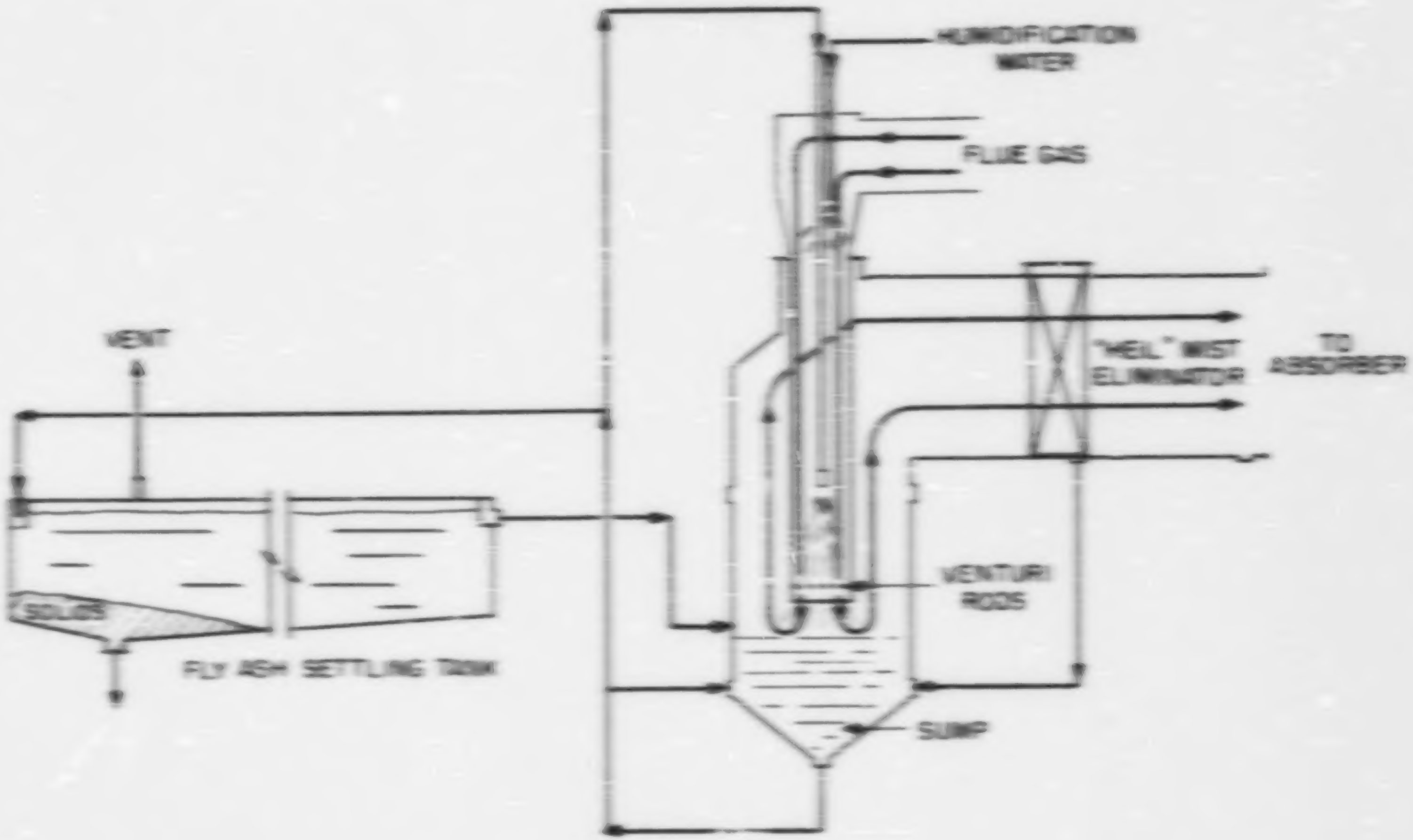

HUMIDIFICATION WATER
FLUE GAS
VENT
"HEIL" MIST ELIMINATOR
TO ABSORBER
SOLIDS
VENTURI RODS
FLY ASH SETTLING TANK
SUMP

Figure 7. Flue gas prewash.

was constructed of 316 SS to withstand the 300°F gas entering the section.

The prewash section was operated in a closed-loop configuration. A settling tank was installed to remove undissolved solids (flyash) from the recirculating prewash liquor. The tank was constructed of FRP and was designed to have a liquor residence time of 8 hr at a liquor throughput rate of 0.5 gpm.

Absorber--

The absorber tower was comprised of three independent absorption stages and one water wash stage, each 32 by 32 by 48 in. high, followed by a Heil chevron mist eliminator in the horizontal section immediately after the vertical tower. During the latter part of the test work, a plastic mesh mist eliminator (Otto H. York Company, Inc.) was installed between the fourth stage and the Heil mist eliminator to improve mist elimination efficiency.

As stated earlier, valve-type tray elements were used to better control the concentration of liquor in each absorber (scrubber) stage. Poor control of liquor concentration was conducive to fume formation. With these trays, falling of liquor from one stage to another or blowing of liquid to an upper stage was not a problem providing the gas flow rate was maintained in a very narrow range. Fall-through was severe when the gas flow was turned down as little as 10% below the optimum flow rate of 2,800 $ft^3$/min (about 6.5 ft/sec). A flow increase of 10% above the optimum rate (rate at which no appreciable amount of liquor was transferred by the gas stream) resulted in liquor being blown up to the next higher stage. Efforts were made to control the gas flow rate at 2,800 acfm at 125°F.

Liquor was recirculated independently to each of the absorber stages. Process makeup water was added to the fourth-stage recirculation tank. The recirculation tanks were arranged so that liquor flowed by gravity from the recirculator tank for G-4 stage to G-3 stage, and so on to G-1 stage. Product liquor was metered from G-1 at a rate to give the desired concentration of product liquor. Most of the makeup $NH_3$ entered the system by sparging into the G-2 stage feed tank. Some $NH_3$ entered the G-1 and G-3 recirculator loops for control purposes.

Gas from the mist elimination section flowed through a flow sensing element, a variable-speed, induced-draft blower, a reheat section, and was exhausted to the atmosphere. The reheat section was comprised of a single-pass tube-and-shell heat exchanger with steam at pressures of up to 300 psig on the tube side. The unit was constructed of 1-in.-diameter, 0.095-in.-wall-thickness tubes made of various materials (see Appendix D, Equipment Evaluation) and had a total of 112.4 ft² of heat transfer area.

During the last operating period (April 1976) the lower two absorber stages were modified to increase absorber efficiency (see later discussion on plume control). A 1-ft depth of mobile plastic spheres (1-in. diameter, 5-g weight) was placed on top of the first two absorber stages (0-1 and 0-2, Fig. 8). A 6-in. 316 SS wire mesh pad was anchored approximately 1 ft above each bed of spheres to prevent excess carryover of liquor from the modified stages. The Murphree tray efficiencies on the stages were about 50% before the modifications and about 92% after the modifications.

## Regeneration Section

The regeneration section was comprised of a heater for control of temperature of the absorber product liquor; an acidulation pot where the liquor was acidulated with $H_2SO_4$ (instead of with $NH_4HSO_4$ since an ammonium sulfate decomposer was not available); a stripper for removing $SO_2$ from the acidulated liquor; a crystallizer for $(NH_4)_2SO_4$; and equipment for preparing the crystals for decomposition to produce $NH_4HSO_4$ and gaseous $NH_3$. Figure 9 shows the flowsheet and equipment for the use of $H_2SO_4$ as acidulant and, as dotted lines, the system with a decomposer.

Acidulation and $SO_2$ stripping during Phase III was studied in two acidulator-stripper units. The first one (Figure 10), which had been used earlier, had a cone mixer for mixing the acid with the absorber effluent. The acidulate dropped into a 1-ft-diameter by 6-ft-high tank in which about 85% of the $SO_2$ in the acidulate was released as an essentially pure gas. The liquid phase containing the remainder of the $SO_2$ gas was fed into a 1-ft diameter by a 6-ft-high cylinder containing 4 ft. of dumped Tellerrette packing where 83% of the remaining $SO_2$ was stripped out with air. As dicussed later, this acidulator-stripper system was replaced with a second system in an attempt to improve removal of $SO_2$ from the ammonium sulfate liquor. The second unit was comprised of a small acid-liquor mixing pot and a 4-in.-diameter by 36-ft-tall stripper (Figure 11). The $H_2SO_4$ and heated absorber product liquor were metered simultaneously to the mixing pot, which had a retention time of about 3 min at the normal product liquor flow rate of 0.4 gpm and acid flow rate required to give an acid ion to ammonium ion [as $(NH_4)_2SO_3$ and $NH_4HSO_3$] mol ratio of 1.05. The acidulated material then flowed through a crossover tube to the stripper column, which contained 30 ft of 1-1/2-in. Tellerrette packing. The stripper was made of plastic pipe (CPVC and plexiglas) and was designed so that 10, 20, or 30 ft of packing could be used as required by the test program. Compressed air was used as the stripping gas.

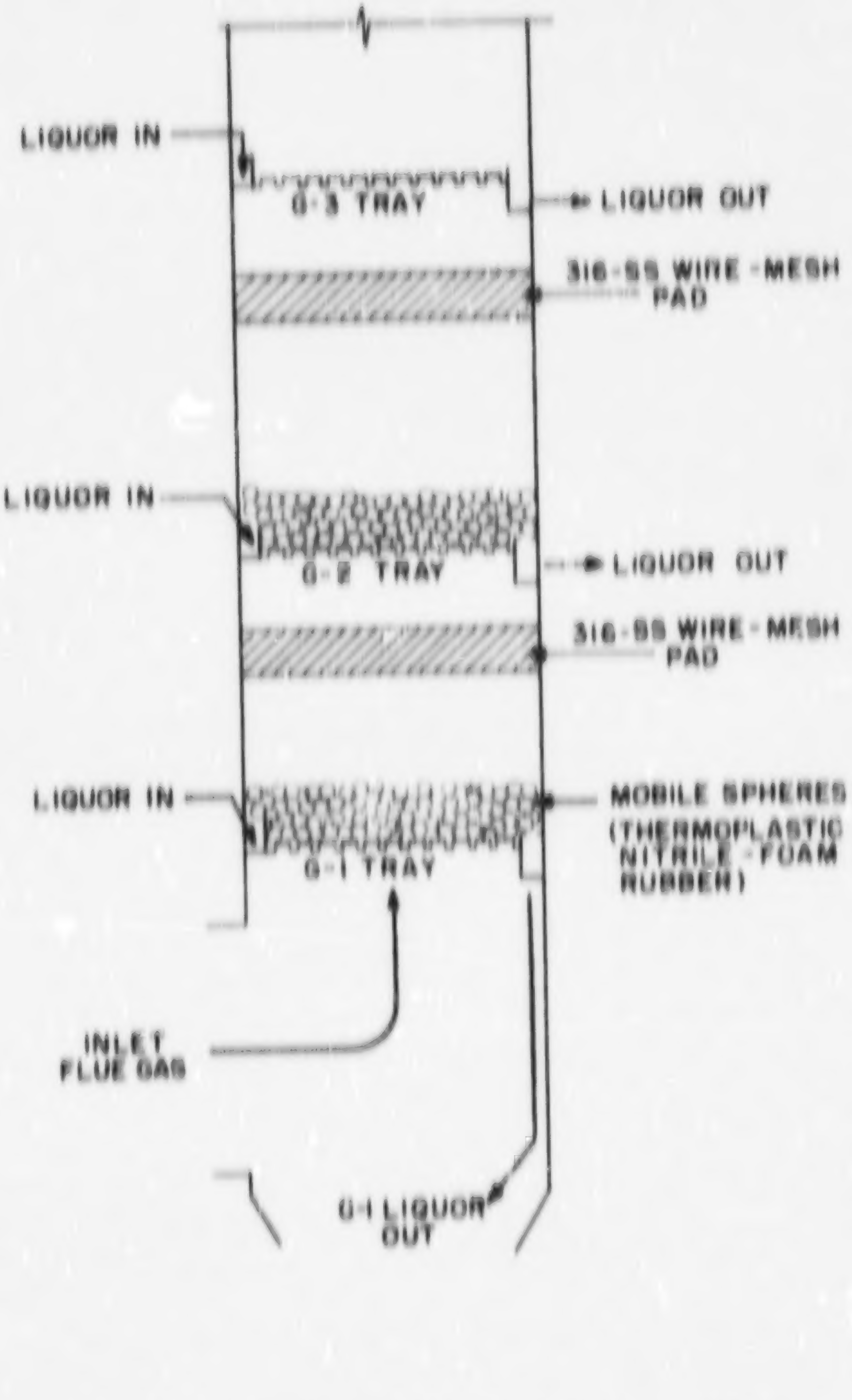

LIQUOR IN
G-3 TRAY
LIQUOR OUT
316-SS WIRE-MESH PAD
LIQUOR IN
G-2 TRAY
LIQUOR OUT
316-SS WIRE-MESH PAD
LIQUOR IN
MOBILE SPHERES (THERMOPLASTIC NITRILE-FOAM RUBBER)
G-1 TRAY
INLET FLUE GAS
G-1 LIQUOR OUT

Figure 8. Modification of absorber to increase efficiency.

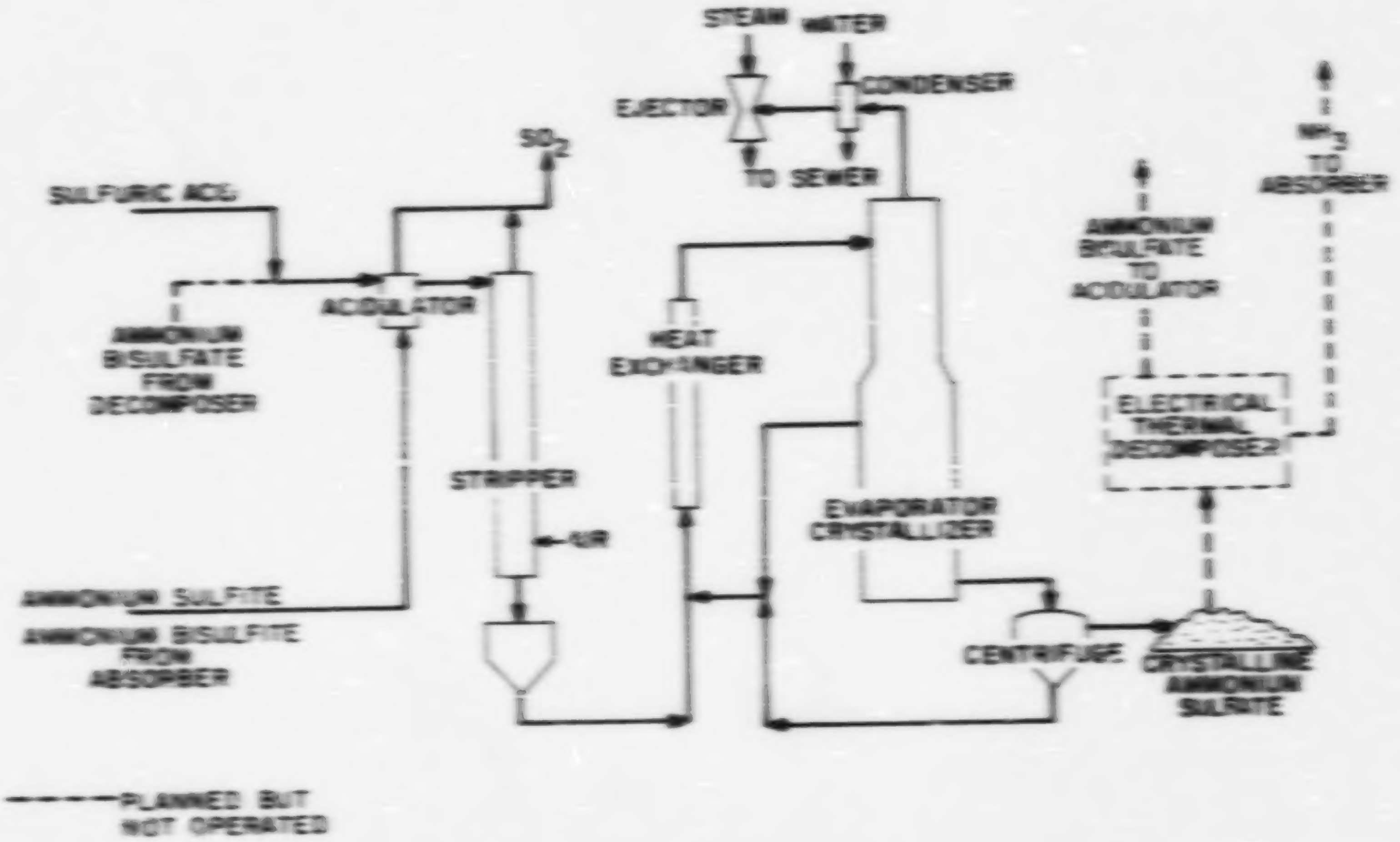

STEAM
WATER
EJECTOR
CONDENSER
TO SEWER
$SO_2$
$NH_3$ TO ABSORBER
SULFURIC ACID
ACIDULATOR
AMMONIUM BISULFATE FROM DECOMPOSER
HEAT EXCHANGER
AMMONIUM BISULFATE TO ACIDULATOR
ELECTRICAL THERMAL DECOMPOSER
STRIPPER
AIR
EVAPORATOR CRYSTALLIZER
AMMONIUM SULFITE
AMMONIUM BISULFITE FROM ABSORBER
CENTRIFUGE
CRYSTALLINE AMMONIUM SULFATE
PLANNED BUT NOT OPERATED

Figure 9. Phase III—Regeneration section

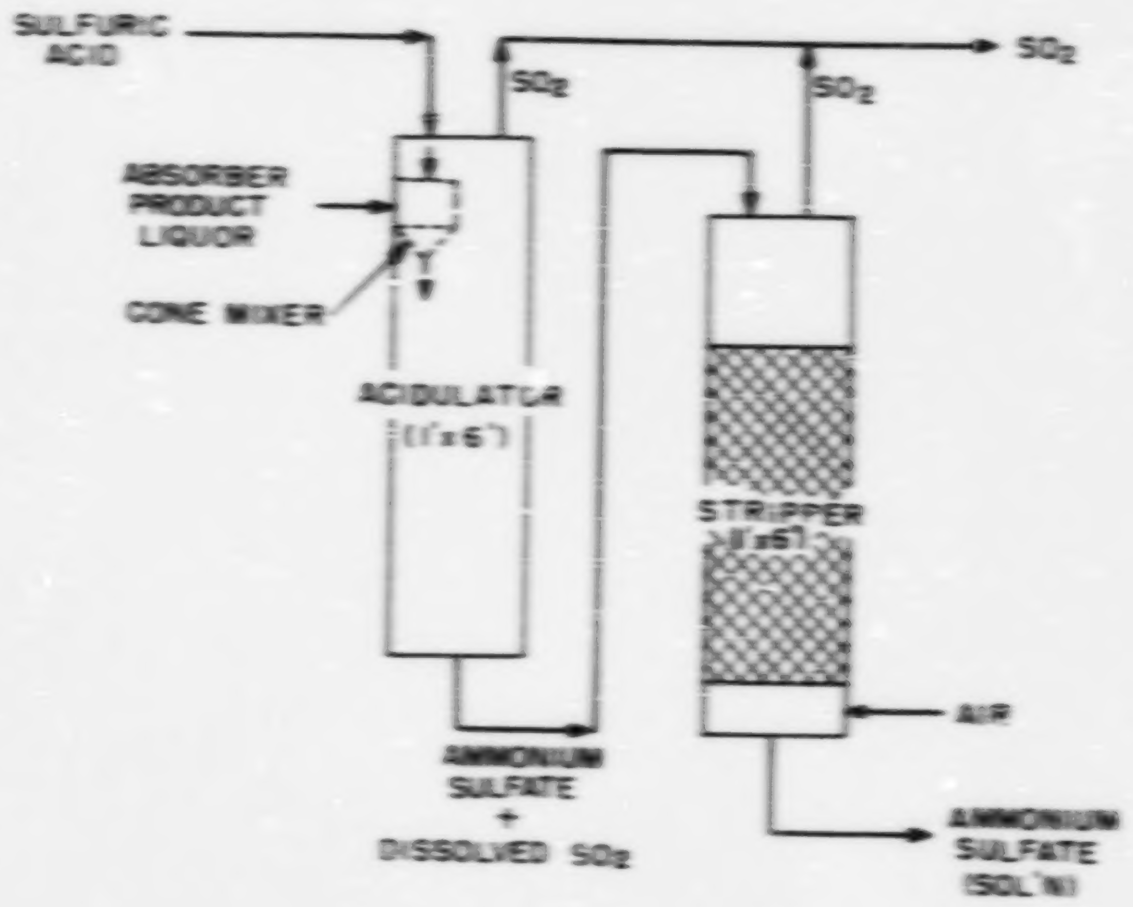

SULFURIC ACID
SO$_2$
SO$_2$
SO$_2$
ABSORBER PRODUCT LIQUOR
CONE MIXER
ACIDULATOR (1'x6')
STRIPPER (1'x6')
AIR
AMMONIUM SULFATE + DISSOLVED SO$_2$
AMMONIUM SULFATE (SOL'N)

Figure 10. First acidulator-stripper.

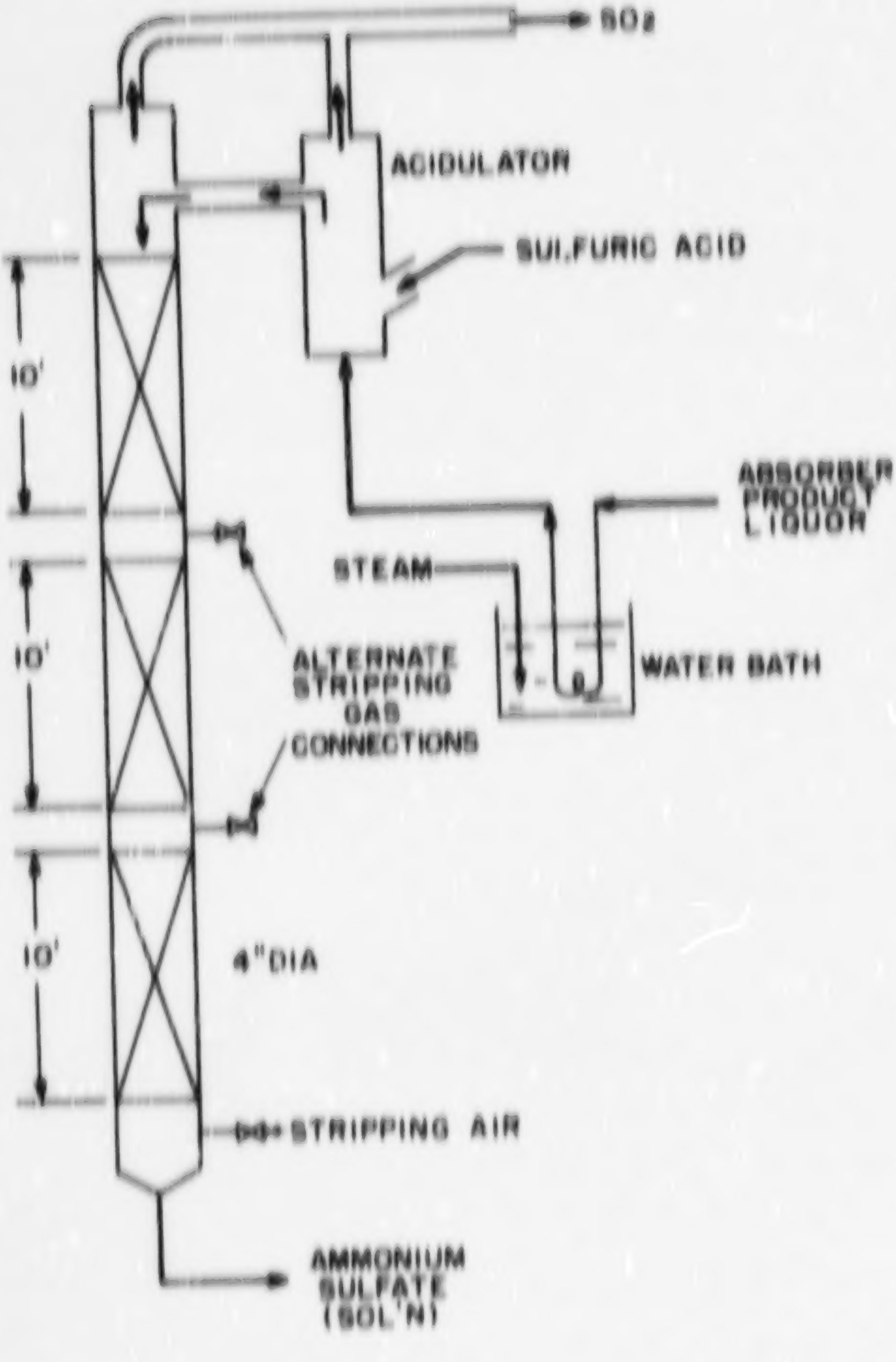

SO2
ACIDULATOR
SULFURIC ACID
10'
10'
10'
ABSORBER PRODUCT LIQUOR
STEAM
WATER BATH
ALTERNATE STRIPPING GAS CONNECTIONS
4"DIA
STRIPPING AIR
AMMONIUM SULFATE (SOL'N)

Figure 11. Final acidulator-stripper.

As shown in Figure 9, the ammonium sulfate solution from the stripper flowed by gravity to a surge-pump tank and was metered to the evaporator-crystallizer (Goslin Inc., Birmingham). The evaporator-crystallizer, made of 316L SS, was designed to remove 200 lb $H_2O$ per hour from a saturated ammonium sulfate solution at about 170°F and under a 22-in. mercury vacuum. Heat was added to the system as steam in a tube-and-shell heat exchanger in the external recirculation loop. A constant-speed centrifugal pump was used to recirculate the brine. A water-cooled condenser and a steam ejector were used to condense the water vapor and to maintain the internal pressure in the system.

A slurry of ammonium sulfate crystals was removed from the evaporator-crystallizer and pumped to a 6-in. screen bowl centrifuge (Bird Machine Co.). The crystals were separated and could, if desired, be dried in a rotary gas-fired dryer. The centrate was returned to the evaporator-crystallizer. Crystals from the ammonium sulfate separation step were to have gone to the ammonium sulfate decomposer which was designed but not constructed.

## Vent System

Exit flue gas from the absorber was vented to the atmosphere for plume observation. The recovered $SO_2$ from the acidulator and stripper was vented into the power plant stack.

## Instrumentation

The pilot plant was instrumented throughout so that all pertinent liquid and gas flows were monitored and values were recorded. All signals were electrically transmitted from the sensing elements to the recorder-controllers.

The gas flow through the absorber system was monitored with a differential pressure cell (The Foxboro Company), which sensed the pressure differential across a flange orifice in the gas duct from the absorber and sent a signal to a recorder-controller. Any deviation from the preset values on the controller-recorder caused a signal to be sent to the variable-speed drive mechanism on the induced-draft blower to correct the deviation. This arrangement assured that a constant gas flow through the absorber system was maintained.

The $SO_2$ concentrations in the gas to the absorber and after each stage were monitored with an ultraviolet analyzer (DuPont's 460 Photometric analyzer). The analyzer has three ranges of $SO_2$ values: 0-4000, 0-1000, and 0-100 ppm full-scale reading. The sample selection was changed manually from station to station to avoid the possibility of leaks from an automatic sample sequencing system. Periodic checks by wet-chemical analysis methods confirmed the analyzer readings. Steam-traced and insulated sample lines (Dekoron) made of Teflon were used to bring samples to the analyzer.

A smoke detector was used to monitor the opacity of the plume at the stack exit. The instrument, manufactured by Photomation, Inc., used a light source and a photocell to measure the plume opacity. The digital readout was in Ringlemann units.

Gaseous $NH_3$ was metered to the system as required with a Foxboro differential pressure cell coupled with a recorder-controller and a flow control valve. Liquid flows were sensed with magnetic flow meters which sent electronic signals to recorder-controllers. The required flows of recirculating liquor to the first three absorber stages were maintained with variable-speed pumps. Variable-speed pumps instead of valves were used for flow control because flyash removed in the bottom stages could cause plugging and erosion of control valves. Automatic flow control valves were used to control the flow of the remaining liquid streams. Air for $SO_2$ stripping was metered to the stripper through rotameters. Temperatures throughout the system were sensed with thermocouples and recorded on strip charts in the control room. (See Appendix D, Equipment Evaluation.)

## ABSORBER TEST PROGRAM AND RESULTS

### Plume Theory and Control Program

Emission of a dense plume from the absorber has plagued all the EPA-TVA pilot-plant work and has been present in full-scale operations that use $NH_3$ to remove $SO_2$ from process gases. Figure 12 shows a typical plume from the pilot plant during routine operation. The plume contained fume particles having a mean diameter of 0.25μ. About $10^7$ particles per cubic centimeter are in the size range of 0.005 to 0.01μ. Figure 13 shows the number-size distribution and Figure 14 shows the mass-size distribution.

The plume particles were identified chemically as predominantly ammonium sulfate with varying amounts (up to 30%) of ammonium chloride. The contribution of ammonium chloride ($NH_4Cl$) to the plume problem was not determined although bench-scale tests, discussed later, did show that chlorides as well as $SO_3$ could contribute to the problem. Flyash also was present in samples of the particulate caught in a modified cascade sampler (Brink sampler).

Conventional wet scrubbers are ineffective in removing extremely small particulate from gas streams. Proposals have been made and actual installations have been built that use electrostatic precipitators or mechanical collectors (impaction

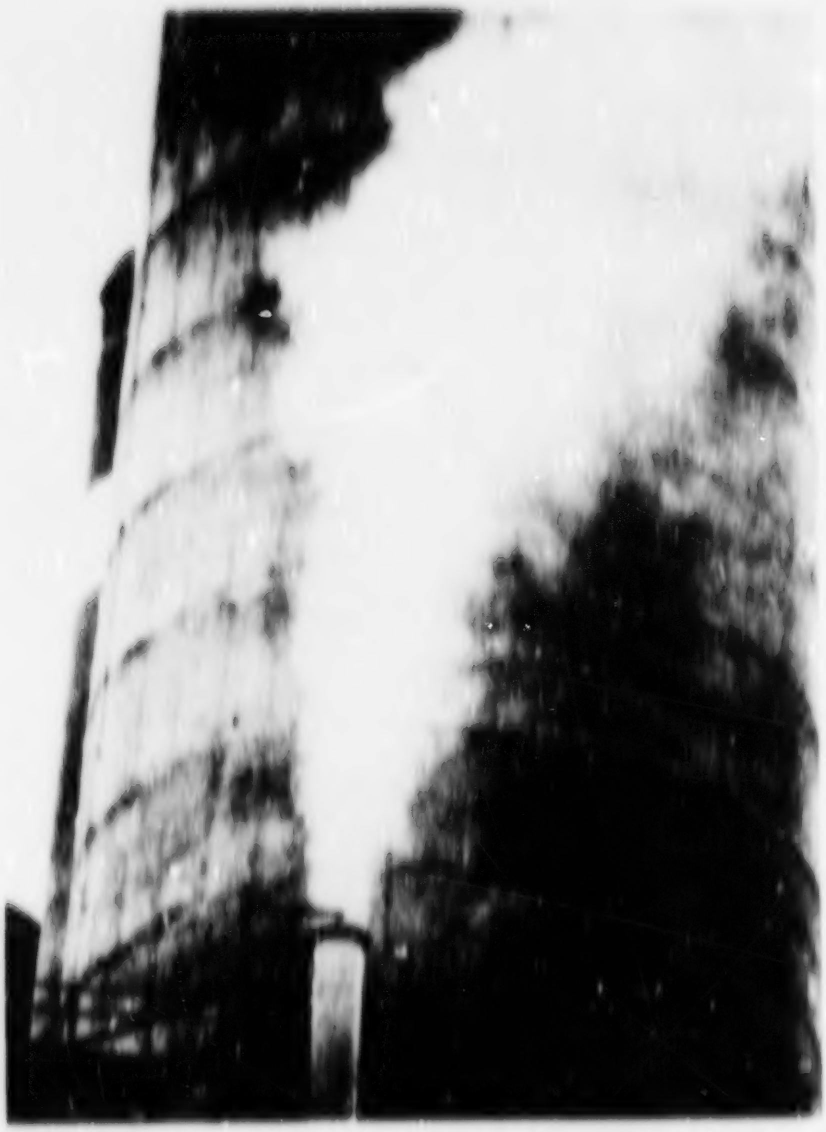


Figure 12. Typical plume from pilot plant.

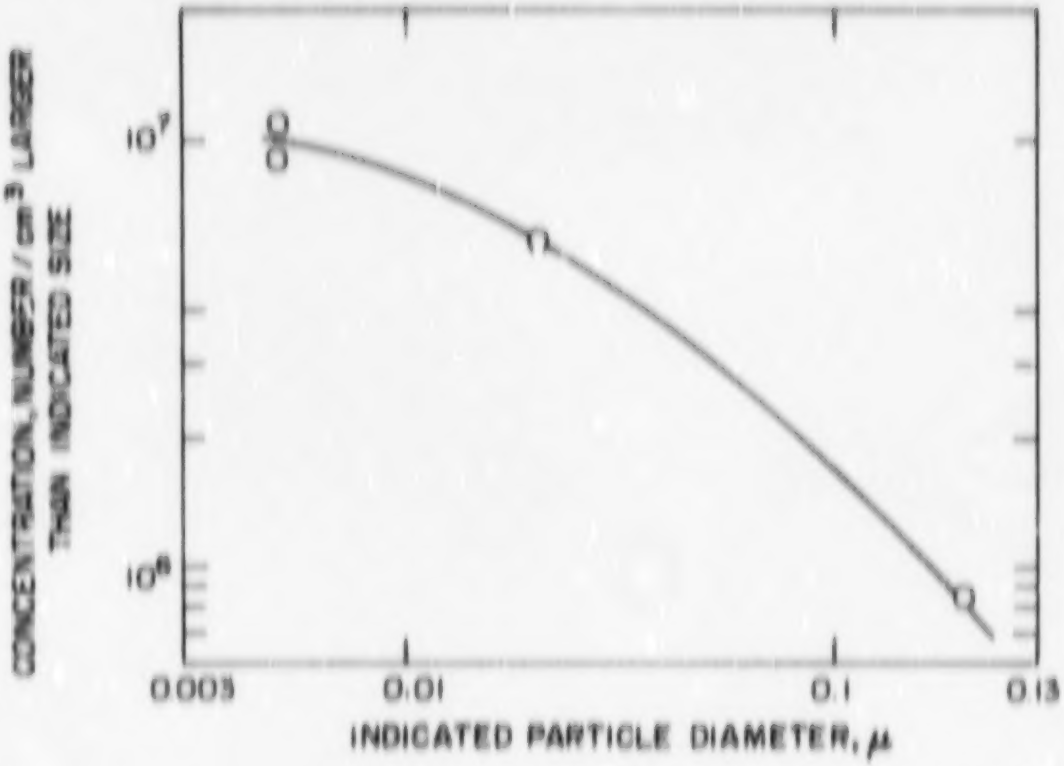


Figure 13. Number - size distribution of particulate in absorber plume.

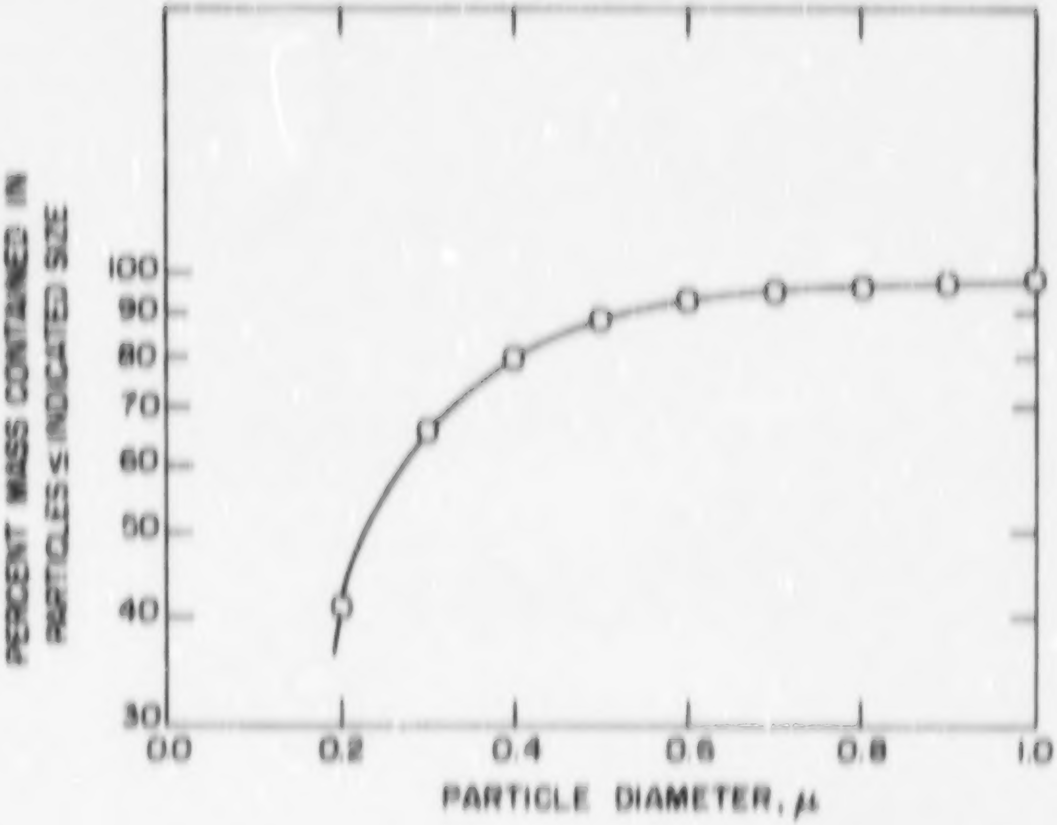


Figure 14. Mass-size distribution of particulate in absorber plume.

devices and bag houses) to remove plume from the washed gas. Unfortunately, the electromechanical methods are expensive and account for a large fraction (about 25%) of the gas cleaning cost.

An approach to plume control that avoids the need for fine particulate removal equipment was proposed by M. L. Spector and P. L. T. Brian(21) of Air Products and Chemicals, Inc., and modified later by R. D. Moore of TVA (see Appendix E). The basis of the proposal is that a gas-phase reaction will produce a solid (fume) whenever the product of the partial pressure of the gases involved exceeds the equilibrium constant for the reaction. The problem then is to avoid absorber operating conditions that allow the gas-phase reaction to occur.

The reaction constant k for a gas-phase reaction can be expressed as a product of the vapor pressures of the constituents. For a compound of the form $A_2B$, the equation for the reaction constant is

$$k = (P_A)^2 (P_B) \qquad (8)$$

The equilibrium constant also can be related to the heat of reaction by

$$\frac{d\ (\ln k)}{dT} = \frac{\Delta H}{RT^2} \qquad (9)$$

where $\Delta H$ = heat of reaction, calories/g mol
$R$ = gas constant, 1.987 calories/(g-mol)(°K)
$T$ = temperature, °K

Assuming $\Delta H$ is constant, integration of equation 9 expressed in terms of $\log_{10}$ gives

$$\log_{10} k = -\frac{\Delta H}{TR(\ln 10)} + I \qquad (10)$$

where I is the integration constant.

The above equation shows that the value for the equilibrium constant for the gas phase reaction is a function of temperature. Spector and Brian evaluated data from in-house experiments and concluded that the gas phase reaction product--fume particle--is solid ammonium bisulfite, $NH_4HSO_3$, and equation 10 is of the form

$$\log_{10} k = \frac{-17{,}300}{T} + 71.4 \qquad (11)$$

where T is in degrees Rankine and k is in mm of mercury.

Moore evaluated data by St. Claire, Earhart, U.S. Bureau of Standards, and Air Products and Chemicals, Inc. He concluded, from the typical ammonia absorption pilot-plant operating conditions, that the fume particles were ammonium sulfite monohydrate [ $(NH_4)_2SO_3 \cdot H_2O$ ] and that equation 8 has the form

$$k = (P_{NH_3})^2(P_{H_2O})^2(P_{SO_2}) \qquad (12)$$

and equation 11 has the value

$$\log_{10}k = -16{,}520/T + 51.35 \qquad (13)$$

where T is in degrees Kelvin and k is in mm of mercury. Moore's treatment of the data and the analysis leading to this conclusion is included in Appendix E of this report.

Taking the $\log_{10}$ of both sides of equation 12 and solving the $\log_{10}P_{SO_2}$, equation 12 becomes

$$\log_{10}P_{SO_2} = \log_{10}k - 2\log_{10}(P_{NH_3})(P_{H_2O}) \qquad (14)$$

where, from Johnstone (6),

$$P_{NH_3} = \frac{M(C_A + 2A)(C_A - S)}{(2S - C_A)} \qquad (15)$$

$$P_{H_2O} = \frac{100\ P_W}{(100 + C_A + S + 3A)} \qquad (16)$$

A in the above equations represents the concentration of $(NH_4)_2SO_4$ (mole per 100 mole of water) in the liquor.

Moore derived an expression for $P_W$, the vapor pressure of pure water over the temperature range of 35 to 60°C as

$$\log_{10}P_W = -2{,}222/T + 8.8403 \qquad (17)$$

Combining equations 12 and 13 and substituting equations 15, 16, and 17, it is possible to calculate a fume value (ppm $SO_2$) for a given set of liquor concentrations. The final form of the fume line equation is

$$\log_{10}P_{SO_2} = -2{,}102/T + 4.3138 + 2\log\left(\frac{(100 + C_A + S + 3A)(2S - C_A)}{(C_A + 2A)\ (C_A - S)}\right) \qquad (18)$$

where T is in degrees Kelvin, and $P_{SO_2}$ is in mm mercury.

## Absorber Tests

### Pilot Plant--

A study plan was developed to test the concept of avoiding the fume problem by controlling the vapor pressures of the gaseous constituents necessary to form the ammonia and sulfur compound fume, namely, ammonia, $SO_2$, and water. The study was carried out under operating conditions indicated by Phase II work to be necessary for fume control. These conditions were:

- A water wash ahead of the absorber
- A water wash after the absorber
- Reheat of the scrubbed flue gas

The water wash ahead of the absorber (prewash section) was used to cool and humidify the gas to prevent localized evaporation of absorber liquor, which would increase the vapor pressure of $SO_2$ or $NH_3$ to a point where gas-phase precipitation would occur. The prewash operation also would remove chlorides and flyash from the flue gas.

In the first prewash unit, which was made of type 316L SS, flue gas entered through a duct in which it was cooled and humidified with a water spray. It then impinged on the surface of a water recirculation sump from which it flowed to the absorber. The unit proved unacceptable because of severe mist carryover and because of excessive corrosion by the recirculated liquor (pH 1-3).

Condensed data from these first fume control tests appear in Appendix F, Table F-1.

A second prewash unit made of corrosion-resistant material and equipped with a mist eliminator was developed and installed. A settling tank also was installed to remove undissolved solids from the recirculating liquor in the closed loop prewash section.

The prewash section was tested with "clean" gas (0.05-0.29 gr flyash/scf) at L/G ratios of 10 and 20 gal/1000 ft³ and at Δp's of 5, 10, and 15 in. $H_2O$ across the venturi element. However, because humidification was not complete at the lower L/G ratio, most of the tests were made with L/G of 20 and Δp's of 10-15 in. $H_2O$. Under the conditions, humidification was essentially complete. Chlorides (as HCl) were decreased in the prewash section from about 45 ppm to 3-7 ppm. This level of chlorides was not expected to cause chloride fuming. "Clean" gas from downstream of electrostatic precipitators was used in all tests. The exit particulate loading from the prewash section was 0.05-0.2 gr/scf, essentially the flyash loading to the prewash section.

Both dissolved and undissolved solids in the recirculating prewash liquor increased with operating time. (Figure 15 shows the undissolved solids versus time, and Figure 16 shows the dissolved solids versus time for the liquor from the settling tank clarifier to the prewash loop.) The solids content had not leveled off at the end of the 9-day sample period, the longest continuous operating period without dilution of prewash liquor. However, replacement of the water lost in the periodic purge of flyash from the settling tank was expected to cause the solids content to level off near the uppermost values shown in Figures 15 and 16. The pH of the liquor in the system was typically 1.0. Chemical analysis of "typical" samples of the prewash liquor is shown in Table 1.

TABLE 1. CHEMICAL ANALYSIS OF PREWASH LIQUOR

| Test No. | PGW-5 |
|---|---|
| Analysis, g/l | |
| Total Fe | 3.8 |
| $Fe_2O_3$ | 1.0 |
| FeO | 3.5 |
| Total S as $SO_4$ | 21.1 |
| Cl | 4.5 |
| Na | 0.08 |
| K | 0.19 |
| Ca | 0.73 |
| Al | 0.75 |
| Solids, % | |
| Dissolved | 3.1 |
| Undissolved | 0.01 |

The mist eliminator, which had been installed in the horizontal duct between the venturi section and the absorber, was highly effective; only traces of water carryover could be found during air-water tests. Tests by EPA personnel during operations with flue gas found mist carryover to be 1 ml/m³ of gas, which was an acceptable level.

The low degree of mist carryover also would lessen the contamination of absorber product liquor by the heavy metals

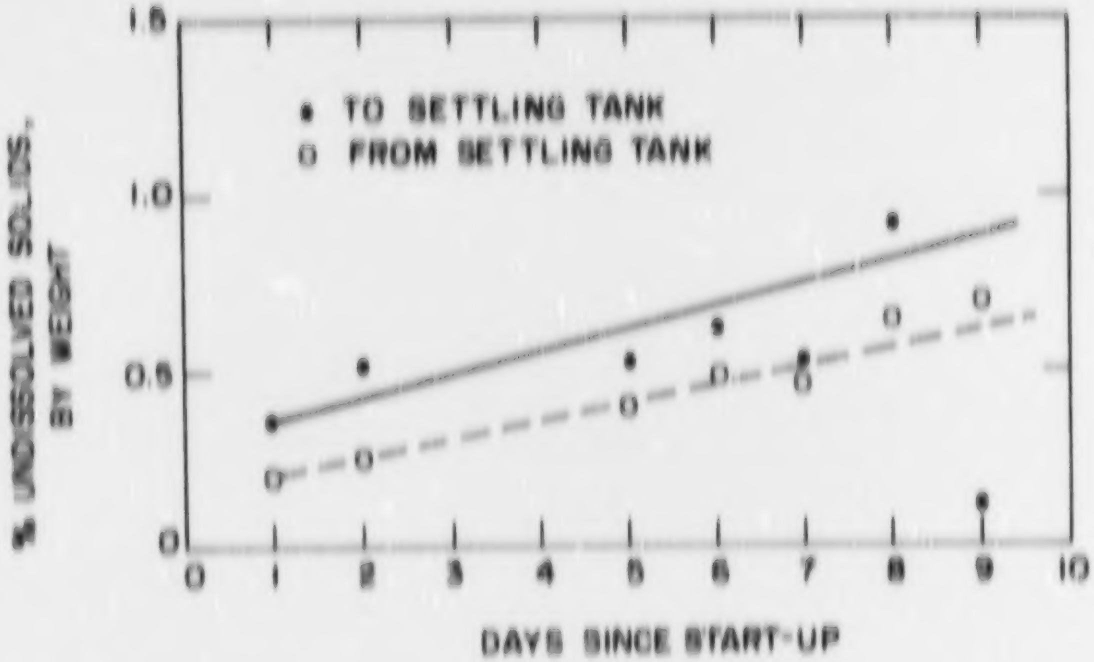


Figure 15. Undissolved solids in prewash liquor to and from settling tank vs. time.

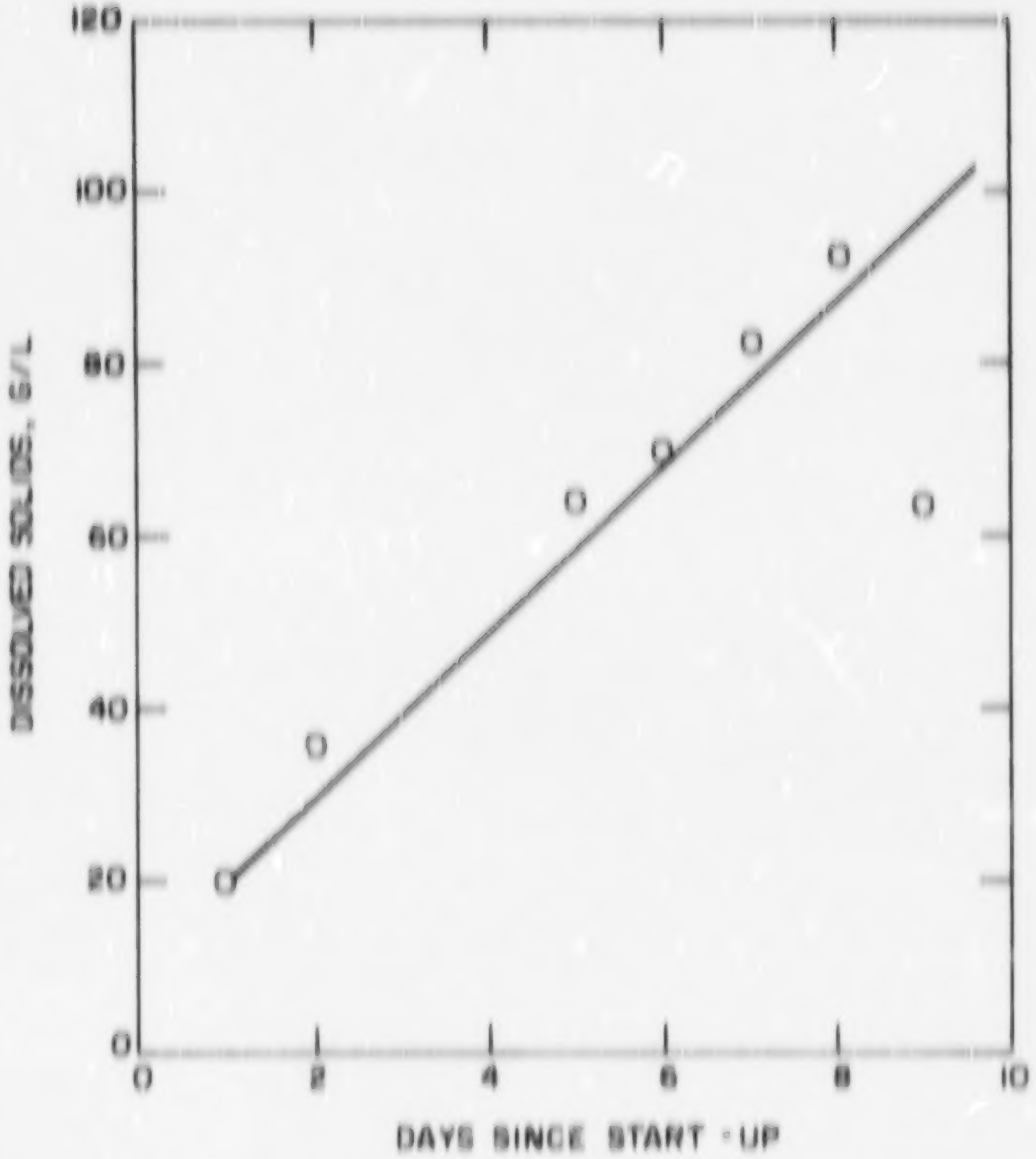


Figure 16. Dissolved solids in prewash liquor from settling tank vs. time.

contained in the flyash. In Phase II work it had been found that the presence of ferrous ammonium sulfite hindered the separation of crystalline $(NH_4)_2SO_4$ in the regeneration step of the process.

Plume control tests were made following the prewash section tests. In these tests the concentration of the absorber product liquor was to be 12 mols active $NH_3$ per 100 mols total water ($C_A$ = 12) and a sulfur to active $NH_3$ mol ratio of 0.80 ($S/C_A$ = 0.8). These values were selected because:

> The concentration was sufficiently high for regeneration purposes; about 2.5 lb of water is evaporated for each pound of recovered $SO_2$.
>
> The ratio of $NH_4HSO_3$ to $(NH_4)_2SO_3$ was 4:1, which minimized the amount of $NH_4HSO_4$ needed for acidulation (2 mols of $NH_4HSO_4$ are required per mol of $(NH_4)_2SO_3$ and 1 mol is required per mol of $NH_4HSO_3$--see equations 5 and 6).
>
> The equilibrium vapor pressure of $SO_2$ above the absorber product solution is such that a large driving force exists between the solution and incoming gas to permit good $SO_2$ removal on the first stage (the equilibrium vapor pressure of $SO_2$ was 0.03 mm Hg while the vapor pressure of $SO_2$ in the inlet flue gas was 2.12 mm Hg).
>
> The $SO_2$ equilibrium vapor pressure is below the fume level as predicted by equation 18.

The desired $S/C_A$ of the liquor on stage G-2 of the modified four-stage absorber was 0.72. This value was selected because it is compatible with the product liquor composition and, because under the conditions expected on stage G-2, equation 18 predicts fumeless operation.

The absorber product liquor $C_A$ was controlled by the amount of makeup water added to stage G-4. The $S/C_A$'s of stages G-1 and G-2 were controlled by the amount and point of addition of makeup ammonia; ammonia could be added to either G-1 or G-2 or both. The liquor composition on G-3 was determined by the requirements of G-1 and G-2. Water only was added to G-4. However, through absorption of $SO_2$ and ammonia from the gas stream and by collecting mist containing $SO_2$-$NH_3$ salts from G-3, the liquor on G-4 at steady-state operating conditions had a $C_A$ of about 2 and an $S/C_A$ of about 0.9. The desired or expected liquor compositions on absorber stages G-1 and G-2 are summarized below:

| Stage | $C_A$ | $S/C_A$ | $A^a$ |
|---|---|---|---|
| G-1 | 12 | 0.80 | 1.75 |
| G-2 | 10 | 0.72 | 1.50 |

a. "A" values, mols of sulfate per 100 mols water, were assumed for calculation purposes.

Using equation 18 the calculated $SO_2$ concentration for formation of the ammonium sulfite monohydrate fume particle at 130°F on stage G-1 is 6,255 ppm.

Similarly, the equation predicts that a fume can form on G-2 when the $SO_2$ concentration to G-2 exceeds 2,399 ppm. Figures 17 and 18 show the calculated fume lines and equilibrium lines for the above-listed absorber liquors over a range of temperatures for stages G-1 and G-2.

For fumeless operation, the vapor pressure of $SO_2$ must be controlled within the area bounded by these lines.

Most of the fume control tests were made at the high liquor concentrations. Some tests were made at low liquor concentrations because, as can be shown by equation 19, formation of a fume is less likely to occur at the low $C_A$'s than at the high $C_A$'s. Condensed data from the tests appear in Appendix F.

Control of the absorber liquor composition was difficult in the four-stage valve-tray absorber (before the use of mobile spheres on the G-1 and G-2 trays). In one series of tests before the absorber was modified (series AX) the absorber liquor $C_A$ varied from a low of 11.6 to a high of 15.5, with 8 of the 11 tests having a $C_A$ of between 11.6 and 12.6. A fluctuation of ±0.5 unit of $C_A$ does not greatly affect the vapor pressure of $SO_2$ and was considered acceptable for the test operation. A fluctuation of ± 0.02 unit of $S/C_A$ has a large effect on $SO_2$ vapor pressure and can move the predicted fumeless operation to the fume region. For instance, the $SO_2$ concentration required to cause fuming as predicted by equation 18 for a solution having a $C_A$ of 12 and an $S/C_A$ of 0.80 and at 125°F is 5,800 ppm. At the same condition, with the $S/C_A$ decreased to 0.78, the predicted fume value is lowered to about 4,200 ppm. Figure 19 shows the effect of deviations of 0.5 unit $C_A$ and 0.02 unit $S/C_A$ from the fume line for a liquor having $C_A$ of 12 and $S/C_A$ of 0.80.

Two of the 11 tests in the AX series (tests AX-4 and AX-5) had observed plumes of 5% opacity or less; all of the others had stack opacities greater than 5%. According to the fume prediction equations, all tests should have produced fumes

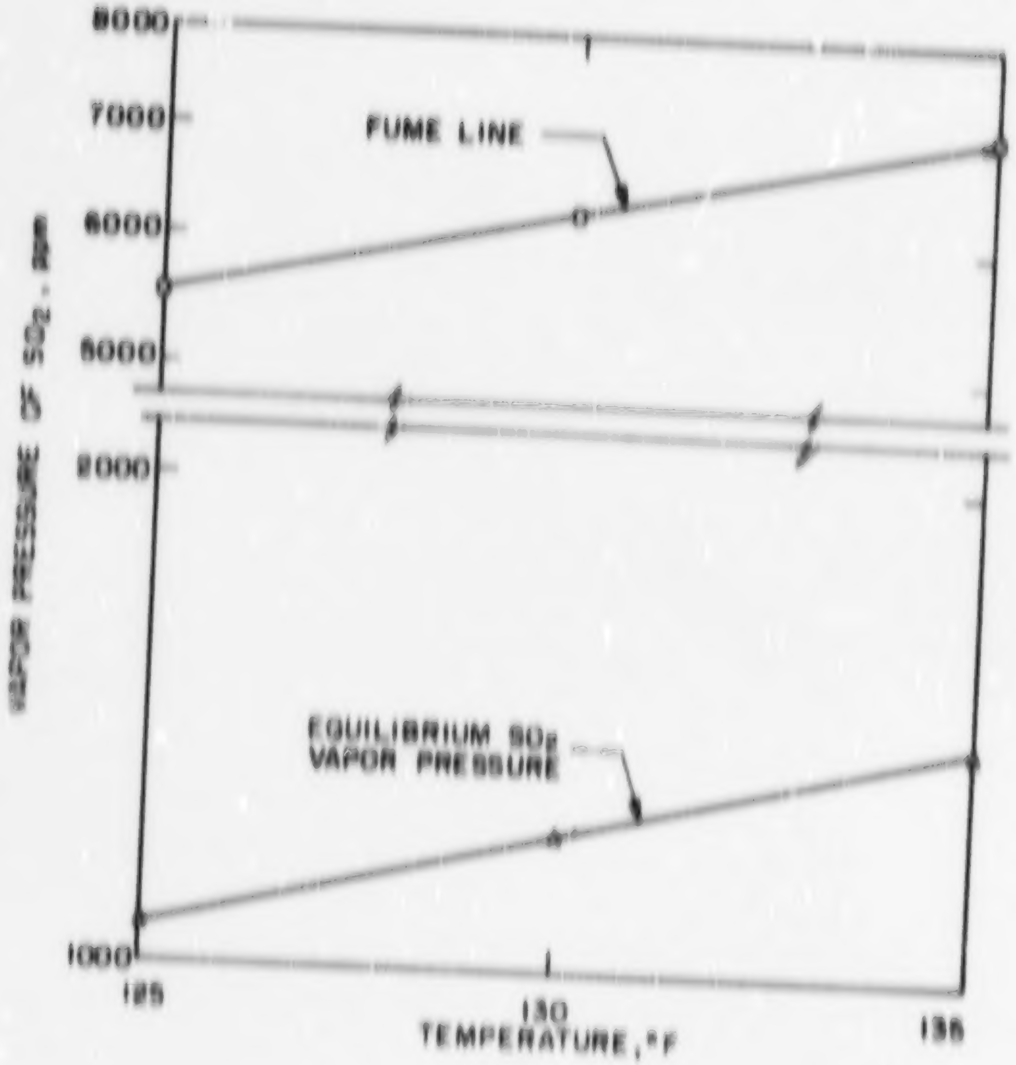


Figure 17. Equilibrium $SO_2$ vapor pressure with respect to the fume line for G-1 stage.

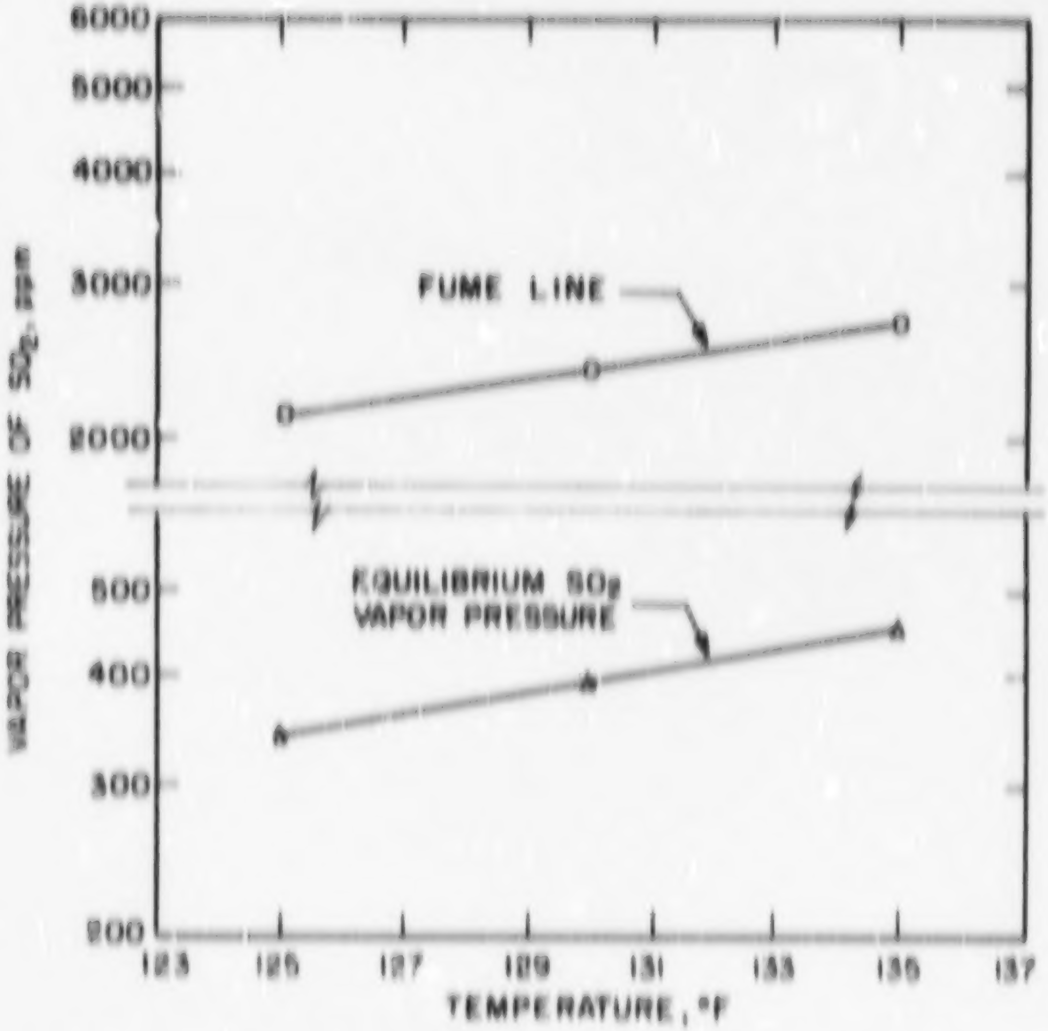


Figure 18 Equilibrium $SO_2$ vapor pressure with respect to the fume line for G-2 stage.

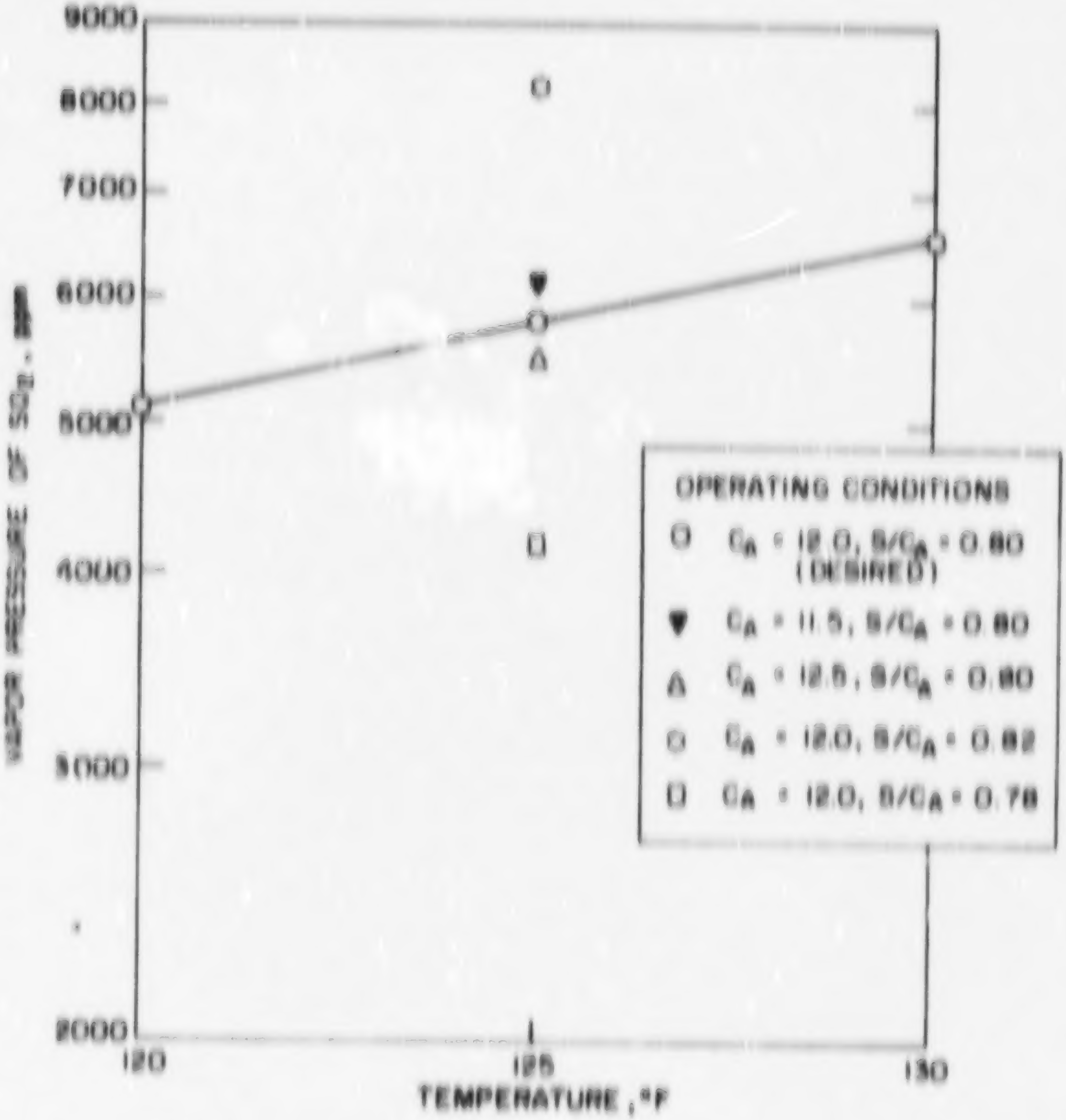


Figure 19 A theoretical fume line with points demonstrating the sensitivity of fume values to deviations of $C_A$ and $S/C_A$.

(Appendix F). No explanation for the low opacity in tests AX-4 and AX-5 could be determined from the data. The temperature of the gas to the prewash section and the temperature of the saturated gas to the absorber were lower in these tests than is normal--less than 200°F as compared with a "normal" temperature of 250-300°F. Several tests were run with inlet gas temperature of 200°F or less without reproducing the results of tests AX-4 and AX-5.

The calculated fuming occurred on stage G-2 in all tests because the $S/C_A$ was below the desired value on G-2 or above the desired value on G-1. A high $S/C_A$ (>0.80) on G-1 results in less $SO_2$ removal on G-1 and more $SO_2$ on G-2. A low $S/C_A$ (>0.72) on G-2 results in a high ammonia vapor pressure and increases the likelihood of fume by increasing the product of the vapor pressures of the constituents. The overall $SO_2$ removal efficiency in the four-stage valve-tray absorber was poor, and additional $NH_3$ was introduced to G-2 in order to reach the arbitrarily set minimum of 80% $SO_2$ removal for this test series. Murphree tray efficiencies for G-1 and G-2 trays ranged from 13.2 to 95% with an average Murphree efficiency of 41.6% on G-1 and 66.1% on G-2.

Prior to the next series of tests (BX series), the two bottom stages of the valve-tray absorber were modified to improve $SO_2$ removal efficiency and to improve control of the liquor concentrations on these two stages. As stated earlier the modification involved adding a 12-in. depth of 1-in.-diameter hollow sphere (5-g weight) to each stage to improve the mass transfer of the stages. The spheres were simply poured onto each stage. A 6-in.-thick wire mesh mist eliminator was anchored 1 ft above the bed of spheres. During operation, liquor from the valve tray irrigated the spheres. The wire mesh pads caught the large volume of mist to prevent its being carried to the next higher stage and disrupting control of the liquor concentration on that stage. The modifications increased the pressure drop by 2 in. of $H_2O$ on both stages G-1 and G-2 (overall pressure drop for the modified absorber was 12 in. $H_2O$). Sulfur dioxide removal efficiency in the modified absorber was improved--the Murphree stage efficiency averaged 90% for G-1 and 92% for G-2 in the BX series.

The desired values of $C_A$ and $S/C_A$ for the BX series were:

| Stage | $C_A$ | $S/C_A$ | $A^a$ |
|---|---|---|---|
| G-1 | 12 | 0.78 | 1.75 |
| G-2 | 10 | 0.72 | 1.50 |

---

a. "A" values assumed for calculation purposes.

It was expected that, under these conditions, the liquor of G-1 would have a $C_A$ of 2 and an $S/C_A$ of 0.80.

The decrease in $S/C_A$ on G-1 for the BX series was made to increase $SO_2$ removal on G-1 and decrease the quantity of $SO_2$ to G-2. Under these conditions and at a temperature of 125°F, 3,958 ppm of $SO_2$ are required to cause a fume, well above the maximum inlet $SO_2$ concentration of 3,400 ppm observed during the test.

The $S/C_A$ selected for stage G-2 was 0.72, the same as for the AX series. The calculated minimum $SO_2$ concentration for fuming on G-2 under these conditions is 1,979 ppm. This gives a safe margin if reasonable Murphree tray efficiencies are achieved because the equilibrium concentration of $SO_2$ to G-2 is 338 ppm.

Data from the BX series also appear in Appendix F. Control of liquor composition was improved over previous work, although in some tests the $S/C_A$ varied more than the 0.02 unit considered acceptable for the test.

Stack opacities of 5% or less were observed during 6 of the 12 sampling periods. However, inconsistencies in the test results were apparent. Shown in Table 2 are selected data from three tests in the BX series. Test BX-11 predicts no plume (5% or less opacity) and the observed opacity was 5%. A plume was predicted for test BX-12 and a plume of 20% was observed. In test BX-10 a plume was predicted but the observed opacity was 5%. No explanation has been found for the inconsistencies.

One series of tests was run in the unmodified absorber in which the washed gas was reheated from the absorber outlet temperature (about 135°F) to 225°F in 10° intervals. The gas was reheated with an in-line indirect tube-and-shell heat exchanger with 350 psig steam on the tube side. (The overall heat-transfer coefficient for the heat exchanger ranged from 14.8 to 27.6 Btu/(hr)(ft²)(°F). Data from these tests appear in Appendix F, Table F-2.

In none of the five tests with plumes at 135°F was the stack opacity made acceptable by increasing the stack gas temperature to 225°F. These tests show that stack gas reheating is not the answer to the ammonia-sulfur compound plume problem.

Typical operating data for the absorption section are shown in Table 1.

## TABLE 2. SELECTED DATA FROM SS SERIES

| Test No. | SS-10 | SS-11 | SS-12 |
|---|---|---|---|
| Liquor concentrations | | | |
| T-1 | | | |
| In | | | |
| $C_A$ | 12.11 | 12.53 | 12.72 |
| $S/C_A$ | 0.80 | 0.79 | 0.80 |
| Out | | | |
| $C_A$ | 11.38 | — | 11.92 |
| $S/C_A$ | 0.85 | — | 0.82 |
| T-2 | | | |
| In | | | |
| $C_A$ | 12.61 | 10.51 | 10.06 |
| $S/C_A$ | 0.69 | 0.72 | 0.68 |
| Out | | | |
| $C_A$ | 12.42 | — | 10.25 |
| $S/C_A$ | 0.88 | — | 0.70 |
| T-3 | | | |
| In | | | |
| $C_A$ | 1.76 | 1.52 | 1.31 |
| $S/C_A$ | 0.95 | 0.91 | 0.89 |
| Out | | | |
| $C_A$ | 2.17 | — | 1.17 |
| $S/C_A$ | 0.85 | — | 0.93 |
| T-4 | | | |
| In | | | |
| $C_A$ | 0.63 | — | |
| $S/C_A$ | 0.95 | — | — |
| Out | | | |
| $C_A$ | 0.69 | — | — |
| $S/C_A$ | 0.98 | — | — |
| Gas temperatures, °F | | | |
| To prewash | 232 | 225 | 226 |
| To T-1 | 122 | 123 | 126 |
| To T-2 | 121 | 121 | 121 |
| To T-3 | 116 | 116 | 117 |
| To T-4 | 115 | 115 | 115 |
| Stack | 185 | 178 | 176 |
| Liquor temperatures, °F | | | |
| T-1 out | 122 | 125 | 121 |
| T-2 out | 120 | 119 | 119 |
| T-3 out | 116 | 116 | 116 |
| T-4 out | 115 | 115 | 115 |
| $SO_2$ concentrations, ppm | | | |
| To T-1 | 2,260 | 2,060 | 2,120 |
| From T-1 | 1,160 | 1,180 | 1,200 |
| Calculated fume on T-1 | 6,161 | 6,217 | 6,161 |
| To T-2 | 1,160 | 1,180 | 1,200 |
| From T-2 | 280 | 300 | 160 |
| To fume on T-2 | 152 | 1,533 | 1,012 |
| To T-3 | 280 | 300 | 160 |
| From T-3 | 260 | 280 | 140 |
| To fume on T-3 | 4 | 4 | 4 |
| To T-4 | 260 | — | — |
| From T-4 | 240 | — | — |
| To fume on T-4 | 4 | — | — |
| Overall $SO_2$ removal, % | 88.6 | 89 | 88 |
| Plume opacity, % | | | |
| Observer | 5 | 5 | 20 |

a: Theoretical calculations show that it is impossible to fume at these tray concentrations.

## TABLE 3. TYPICAL ABSORBER TEST DATA

| | |
|---|---|
| Flue gas to prewash | |
| Flowrate, scfm at 32°F | 2350 |
| Temperature, °F | 325 |
| $SO_2$, ppm | 2640 |
| Flyash, gr/scf | 2 |
| Flue gas to absorber | |
| Flowrate, acfm | 2800 |
| Temperature, °F | |
| Wet bulb | 123 |
| Dry bulb | 124 |
| $SO_2$, ppm | 2640 |
| Flyash, gr/scf | 0.5 |
| Flue gas leaving G-1 stage | |
| Temperature, °F | 121 |
| $SO_2$, ppm | 1180 |
| Flue gas leaving G-2 stage | |
| Temperature, °F | 116 |
| $SO_2$, ppm | 390 |
| Flue gas leaving G-3 stage | |
| Temperature, °F | 115 |
| $SO_2$, ppm | 290 |
| Flue gas leaving G-4 stage | |
| Temperature, °F | 115 |
| $SO_2$, ppm | 280 |
| Flue gas leaving stack | |
| Temperature, °F | 178 |
| $SO_2$, ppm | 285 |
| $NH_3$, ppm | 20 |
| Overall $SO_2$ removal, % | 89 |
| Plume opacity, % | 5 |
| Absorber liquors | |
| Temperature, °F | |
| To G-1 | 123 |
| To G-2 | 116 |
| To G-3 | 115 |
| To G-4 | 115 |
| Composition | |
| To G-1 | |
| $C_A$ | [illegible] |
| $S/C_A$ | 0.78 |
| pH | 6.0 |
| Sp.gr. | 1.225 |
| To G-2 | |
| $C_A$ | 10.73 |
| $S/C_A$ | 0.72 |
| pH | 6.2 |
| Sp.gr. | 1.180 |
| To G-3 | |
| $C_A$ | 3.12 |
| $S/C_A$ | 0.81 |
| pH | 5.7 |
| Sp.gr. | 1.060 |
| To G-4 | |
| $C_A$ | 0.70 |
| $S/C_A$ | 0.60 |
| pH | 4.8 |
| Sp.gr. | 1.025 |

The absorber was operated with low liquor concentrations to determine whether fume would form with low ammonia vapor pressure in the absorber. (These tests were made at the beginning or end of a high $C_A$ test series.) Liquor with $C_A$'s in the range of 0.5-1.5 was produced. From equation 18, it would be predicted that no fume is possible when operating with a $C_A$ of 1 and an $S/C_A$ as low as 0.58. Except for one isolated sampling period (test RX-12), the observed plume opacities were 5% or less for all four-stage absorber operations at the low concentrations.

The results of the plume tests at concentrations acceptable for the ammonium bisulfate process (or for production of crystalline ammonium sulfate) indicate that the thermodynamic equations are useful in predicting regions of fumeless operation. However, satisfying the equations is a necessary but not total requirement for fumeless operation. Also, the equations do not consider fumes that may occur from chlorides and $SO_3$ reacting with ammonia. Further developmental work on a large scale does not appear warranted.

Bench Scale--

A bench-scale sample train of six glass wash bottles was set up to investigate fume formation. The first two wash bottles were used as a prewash section, the third was dry for mist fallout, the fourth bottle was used as an ammoniacal liquor absorption section ($NH_4OH$), and the last two were filled with hydrogen peroxide for removing $NH_3$ and $SO_2$ from the gas before it passed into the gas flow meter. Fuming sulfuric acid (20% oleum), 20% hydrochloric acid, deionized water, and 80% isopropyl alcohol solution were used as scrubbing media. Clean flue gas (0.2 gr/scf), dirty flue gas (5 gr/scf), bottled gas of known concentration ($SO_2$ span gas, 950 ppm $SO_2$), or air was pulled through the sample train. A filter system for particulate removal was inserted at various points in the sampling train. A Gelman Instrument Company fiberglass "absolute" filter, type E, was used in the filter system. The filter removed 99.7% of 0.3μ particles and 98% of 0.05μ particles. Table 8 lists the various test conditions and test results.

A fume was formed in all tests with flue gas whenever the absolute filter was excluded from the sampling train. Whenever the absolute filter was used anywhere in the system, a fume did not leave the system; if the filter was located before the ammoniacal solution, no fume formed; if the filter was after the ammoniacal solution, a fume formed but was removed by the filter. The prewash section prevented fume from forming for 15-20 min

## TABLE 4. BENCH-SCALE TEST CONDITIONS AND RESULTS

| Test No. | Gas used | Position 1 | Position 2 | Position 3 | Position 4 | Position 5 | Position 6 | Position 7 |
|---|---|---|---|---|---|---|---|---|
| [illegible] | Clean stack gas | Filter | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(no flame) | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Clean flue gas | – | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(dense flame) | Dry<br>(dense flame) | [illegible] $H_2O_2$<br>(dense flame) | [illegible] $H_2O_2$<br>(dense flame) |
| [illegible] | Clean flue gas | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(dense flame) | Filter | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Clean flue gas | Filter | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(no flame) | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Clean flue gas | – | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(slight flame) | Dry<br>(slight flame) | [illegible] $H_2O_2$<br>(slight flame) | [illegible] $H_2O_2$<br>(slight flame) |
| [illegible] | Clean flue gas | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(slight flame) | Filter | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Dirty stack gas | Filter | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(no flame) | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Dirty flue gas | – | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(slight flame) | Dry<br>(slight flame) | [illegible] $H_2O_2$<br>(slight flame) | [illegible] $H_2O_2$<br>(slight flame) |
| [illegible] | Dirty flue gas | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(slight flame) | Filter | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Dirty flue gas | Water<br>(no flame) | [illegible]<br>(no flame) | [illegible] $NH_4OH$<br>(slight flame) | Filter | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Span gas<br>[illegible] ppm $SO_2$ | – | Water<br>(no flame) | Water<br>(no flame) | [illegible] $NH_4OH$<br>(no flame) | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Span gas<br>[illegible] ppm $SO_2$ | – | Dry | Dry | [illegible] $NH_4OH$<br>(no flame) | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |
| [illegible] | Span gas<br>[illegible] ppm $SO_2$ | [illegible] HCl<br>(no flame) | [illegible] HCl<br>(no flame) | [illegible] $NH_4OH$<br>(flame) | Dry<br>(flame) | [illegible] $H_2O_2$<br>(flame) | [illegible] $H_2O_2$<br>(flame) | – |
| [illegible] | Span gas<br>[illegible] ppm $SO_2$ | [illegible] HCl<br>(no flame) | [illegible] HCl<br>(no flame) | [illegible] $NH_4OH$<br>(flame) | Filter | Dry<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) | [illegible] $H_2O_2$<br>(no flame) |

(continued)

TABLE 4. (Continued)

| Test No. | Gas Used | Position 1 | Position 2 | Position 3 | Position 4 | Position 5 | Position 6 | Position 7 |
|---|---|---|---|---|---|---|---|---|
| PS-7C | Air | 12N HCl<br>(no fume) | 12N HCl<br>(no fume) | 5N $NH_4OH$<br>(fume) | Filter | Dry<br>(no fume) | 5N $H_2O_2$<br>(no fume) | 5N $H_2O_2$<br>(no fume) |
| PS-8B | Span gas<br>950 ppm $SO_2$ | 12N HCl<br>(no fume) | 12N HCl<br>(no fume) | — | 5N $NH_4OH$<br>(fume) | 5N $H_2O_2$<br>(fume) | 5N $H_2O_2$<br>(fume) | — |
| PS-8C | Span gas<br>950 ppm $SO_2$ | 12N HCl<br>(no fume) | 12N HCl<br>(no fume) | Water<br>(no fume) | 5N $NH_4OH$<br>(no fume) | 5N $H_2O_2$<br>(no fume) | 5N $H_2O_2$<br>(no fume) | — |
| PS-9A | Air | 23N oleum<br>(acid fume) | 5N $NH_4OH$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | — | — | — |
| PS-9B | Air | 23N oleum<br>(acid fume) | Water<br>(slight fume) | 5N $NH_4OH$<br>(slight fume) | 5N $H_2O_2$<br>(slight fume) | 5N $H_2O_2$<br>(slight fume) | — | — |
| PS-9C | Air | 23N oleum<br>(acid fume) | Water<br>(slight fume) | Water<br>(slight fume) | 5N $NH_4OH$<br>(slight fume) | 5N $H_2O_2$<br>(slight fume) | 5N $H_2O_2$<br>(slight fume) | — |
| PS-9D | Air | 23N oleum<br>(acid fume) | Filter | 5N $NH_4OH$<br>(slight fume) | 5N $H_2O_2$<br>(slight fume) | 5N $H_2O_2$<br>(slight fume) | — | — |
| PS-9E | Air | 23N oleum<br>(acid fume) | 5N $NH_4OH$<br>(dense fume) | Filter | 5N $H_2O_2$<br>(no fume) | 5N $H_2O_2$<br>(no fume) | — | — |
| PS-12A | Air | 23N oleum<br>(acid fume) | 97% $H_2SO_4$<br>(dense fume) | Water<br>(dense fume) | 5N $NH_4OH$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | — |
| PS-12B | Air | 23N oleum<br>(acid fume) | Water<br>(fume) | 5N $NH_4OH$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | 97% $H_2SO_4$<br>(slight fume) | — |
| PS-12C | Air | 23N oleum<br>(acid fume) | Water<br>(fume) | 5N $NH_4OH$<br>(dense fume) | 97% $H_2SO_4$<br>(slight fume) | 5N $H_2O_2$<br>(dense fume) | 5N $H_2O_2$<br>(dense fume) | — |

while clean flue gas was used. When silver nitrate was added to the water, a white precipitate formed, which indicated the presence of chloride or sulfate ions or both.

Fume did not form when $SO_2$ span gas was pulled through a train of deionized water, ammonium hydroxide, and hydrogen peroxide. When the deionized water was replaced with 10% hydrochloric acid solution, a fume formed with either span gas or air. An absolute filter inserted into the train downstream from the ammonium hydroxide impinger removed the fume.

When 20% oleum was substituted for the deionized water and air was pulled through the train, a dense fume formed. A water wash between the oleum impinger and the remainder of the train decreased the severity of the fume. An absolute filter also decreased the severity of the fume but did not completely clear the gas stream.

The bench-scale studies showed that the flue gas contained one or more materials that may cause the formation of fume. The material could be chloride or $SO_3$. Other material such as flyash (which could serve as sites on which the plume particles grow) or organic materials may also cause formation of fume. The tests also showed that the material required for fume formation can be removed ahead of the absorber with a filter that removes submicron particles. Further bench-scale work is needed to identify the fume agent.

## REGENERATION TEST PROGRAM AND RESULTS

### Acidulation and Stripping

As previously stated, the acid source in the ABS process is $NH_4HSO_4$ obtained by decomposing $(NH_4)_2SO_4$. Because the thermal decomposer was not constructed, $H_2SO_4$ was used in the pilot-plant study of the acidulation step. Chemically, this substitution is valid because in solution, a mixture of $H_2SO_4$ and $(NH_4)_2SO_4$ would differ from an $NH_4HSO_4$ solution only by the $SO_4:NH_3$ ratio. This difference was not expected to alter the test results at the concentrations used in the study.

The purpose of the acidulation and stripping tests was to develop techniques that would result in removing essentially all of the absorbed $SO_2$ from the absorber product liquor. A limit of 0.5 g/l of $SO_2$ remaining in the stripped liquor $(NH_4)_2SO_4$ solution was arbitrarily set for the test program. This low limit was set because any $SO_2$ remaining in the solution to the evaporator-crystallizer would be stripped from the solution there and cause pollution problems in the condensate and gases leaving this unit. By the same token, under-acidulation would increase the sulfites to the evaporator-crystallizer where they could either be decomposed to $SO_2$ and stripped from the solution or else be disproportionated to sulfates that would have to be removed from the system. A series of tests was made in the "short" (1-ft-diameter by 6-ft high) acidulator and stripper. The acid ion to ammonia ion mol ratio was varied from 1.04 to 1.85 to determine its effect on $SO_2$ removal. The acid and product liquor were combined in the cone mixer in the top of the acidulator. The retention time in the acidulator was approximately 10 min. The liquor overflowed into the stripper which contained a 4-ft packed bed. The stripping gas (air) flow rate was varied from 5 to 15 ft³/min. The data from these tests are shown in Appendix B, Table B-5. Figure 20 shows the overall $SO_2$ removal efficiency versus acid to ammonia ion mol ratio in the acidulation and stripping equipment. At a ratio near 1.0, the overall $SO_2$ recovery efficiency was about 50%. When the ratio was increased to approximately 1.8, the efficiency was about 96%; at this ratio, the solution contained 5.1 g $SO_2$ per liter. Extrapolation indicated that a ratio of 2.0 would be needed to reach a removal efficiency of 100%. Over the range tested, the stripping air flow rate had little effect on removal of $SO_2$ from the acidulated solution.

Extrapolation of the data obtained in tests with this equipment indicated that an excessively high acid ion to ammonia ion ratio (about 2.0) would be required to reach the 0.5 g/l limit set for the test program (99.5% of the absorbed $SO_2$ must be removed from the solution to meet this goal). The excess acid would place an added load on equipment and present severe corrosion problems, particularly in the evaporator-crystallizer. If the acid were neutralized ahead of the evaporator-crystallizer, the added $(NH_4)_2SO_4$ would have to be removed and decomposed to the acid $NH_4HSO_4$, which would place added energy requirements on the system.

Much better results were obtained with a redesigned acidulator-stripper unit. The original acidulator was replaced with a simple mixing vessel. The new stripper was 4 in. in diameter and contained 10 ft of dumped Tellerette packing. The initial tests with the unit were made in a batchwise mode. Thirty gallons of absorber product liquor was acidulated to a final acid ion to ammonia ion ratio of 1.05 over a period of 15 min. The acidulated material was held in the reaction vessel for an additional 15 min before it was fed to the stripper. The acidulate was heated to 140°F, the calculated equilibrium temperature, when acidulating with $NH_4HSO_4$, and metered to the stripper at a flow rate of 0.5 gpm to approximate the rate that liquor is produced in the absorption section. The 0.5-gpm rate corresponds to a packing irrigation rate of 5.7 gal/(min)(ft²) of packing cross-sectional area. Air was fed to the bottom of the stripper at flow rates of 5, 10, and 15 ft³/min, corresponding to

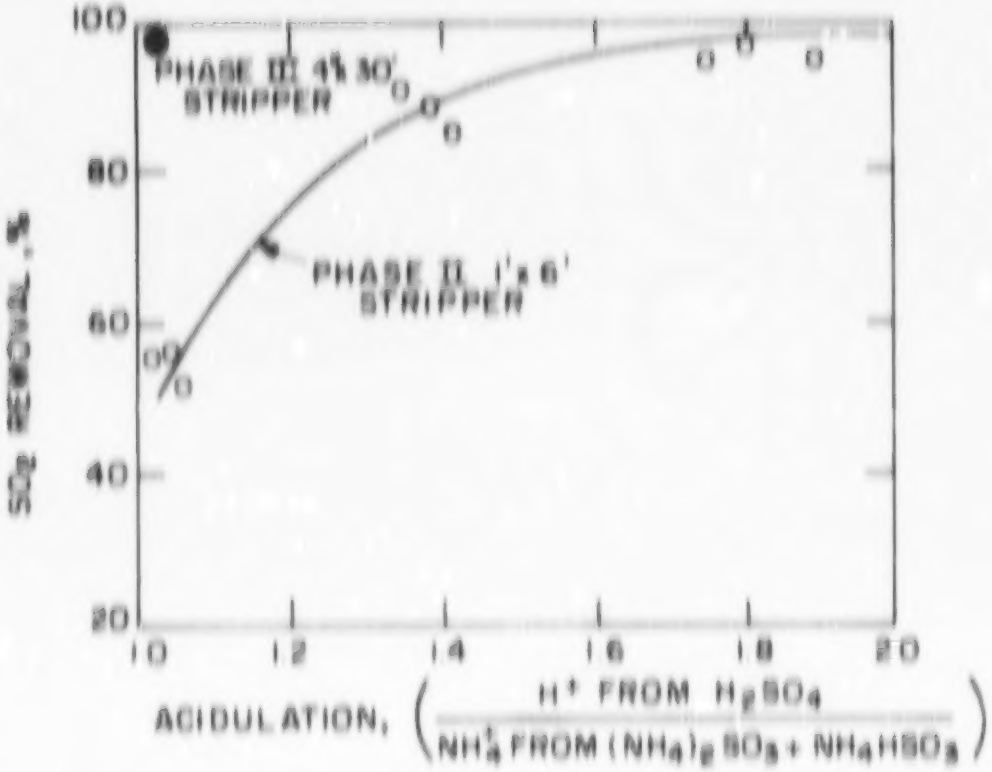


Figure 20 Phase III – $SO_2$ removal from acidulated and stripped liquor vs acidulation.

stripping gas flow rates of 10, 20, and 30 ft³/(min)(gal) of acidulated material.

The results of these tests, AS-1, AS-2, and AS-3, are shown in Appendix F, Table F-6. The acid to ammonia ion ratio was approximately 1.0 in the first two tests and 1.15 in the third. The stripping gas flow rate was 5, 10, and 15 ft³ for tests AS-1, AS-2, and AS-3 respectively. The stripper effluent from these three tests contained free $SO_2$ in excess of the 0.5 g/l; in test AS-3, the $SO_2$ was decreased to 0.68 g/l. The acidulated and stripped liquor was stripped again in test AS-3A using an air feed rate of 15 ft³. The $SO_2$ was decreased to 0.12 g/l on second passage through the stripper, which indicated the need for additional packing height or a higher stripping gas flow rate.

In these batchwise tests, the $H_2SO_4$ was added slowly (about 0.3 gpm) to a large volume of absorber product liquor (30 gal). Near the beginning of the acidulation process, the acid ion to ammonia ion ratio was near zero because of the differences in volumes. The reaction at the point of acid-solution contact was violent and gases flashed off rapidly. As the amount of acid increased, the ratio approached the desired value of 1.05. The violent release of gases decreased with the increase in acid level in the solution and little evidence of gas release was noticeable after about 1/2 to 3/4 of the acid had been added. Since the acidulation was not mechanically agitated, thorough acidulation may not have occurred, even at acid ion to ammonia ion ratios greater than 1.0.

Continuous acidulation was attempted in test AS-4, in which absorber product liquor and sulfuric acid were fed continuously and directly to the stripper. The feed rates approximated full-scale continuous pilot-plant operation. The direct acidulation in the stripper was tried because (1) it permitted continuous operation, (2) it eliminated a piece of process equipment, and (3) gases flashing from the solution would be swept away instead of being reabsorbed in the solution. A violent reaction at the point of addition resulted in the liberation of much heat. In one instance, the temperature rose to 155°F, which is above the design temperature for the plastic stripper. Heavy foaming at the point of addition resulted in surges of flow through the stripper. Sulfur dioxide retained in the stripper effluent was 14.3 g/l.

The procedure for continuous acidulation and stripping was tested further in the final system, Figure 11. The acid and absorber product liquor were fed simultaneously to the bottom of a mixing pot, which overflowed to the top of the stripper. The pot had an effective volume of 1.5 gal, which gave a residence time of about 3 min.

Introduction of acid and liquor into a heel of partially acidulated material reduced the violence of the reaction although some degasing was occurring as the material entered the top of the stripper. Tests were run using an airflow rate of 5 ft³/min (10 ft³/gal of liquor) and the full 30 ft of stripper packing. Data from these tests, AS-6, AS-8, and AS-9, appear in Appendix F, Table F-7. The $SO_2$ retained in the stripped liquor was below 0.5 g/l for each of these tests (0.44, 0.40, and 0.40 g/l respectively). The acid ion to ammonia ion ratio was 1.05 for test AS-6, 1.13 for test AS-8, and 1.15 for test AS-9.

Since the limit of 0.5 g/l $SO_2$ in the stripped liquor could be met in the 30-ft stripper at the 5 ft³ airflow rate, tests were made to determine whether the tower could be shortened and still meet the $SO_2$ limit with stripping gas rates of up to 15 ft³ (30 ft³/gal of liquor).

Tests AS-10, AS-11, and AS-12 were made with 5, 10, and 15 ft³ airflow rates, respectively, with an effective tower packing height of 20.3 ft. Data from these tests appear in Appendix F, Table F-7. In each of these tests, the retained $SO_2$ exceeded the 0.50 g/l limit although in test AS-12 with the 15 ft³ stripping gas flow rate, the retained $SO_2$ was 0.54 g/l. The effect of stripping gas flow rate on retained $SO_2$ is shown in Figure 21.

Since the stripping operation did not reach the desired limit with the 20-ft packing, no tests were made using 10 ft of packing.

The results of acidulation and stripping tests showed that a mixing-pot acidulator coupled with a 30-ft stripper is adequate to reach 0.5 g/l retained $SO_2$ in the stripped liquor with as low as 5 ft³/min stripping gas flow rate. Operation with a 20-ft tower and a 15 ft³/min stripping gas flow rate would be marginal.

The lower stripping gas flow rate results in a higher $SO_2$ concentration in the off-gas (56% for the 5 ft³ rate and 27% for the 15 ft³ rate) though either gas would be acceptable for $H_2SO_4$ manufacture. The nominal $SO_2$ concentration in the sulfur burner off-gas feed stream to a contact $H_2SO_4$ plant is 8.5%.

Table 5 shows typical data from tests meeting the 0.5 g/l limitation for $SO_2$ retained in the stripped liquor.

Ammonium Sulfate Crystal Separation

The ammonium sulfate solution from the acidulation and stripping step was concentrated in an evaporator-crystallizer to produce crystals of $(NH_4)_2SO_4$. The evaporator-crystallizer, manufactured by Goslin-Birmingham, was designed to remove 200 lb/hr of water from the solution. The performance of the single-

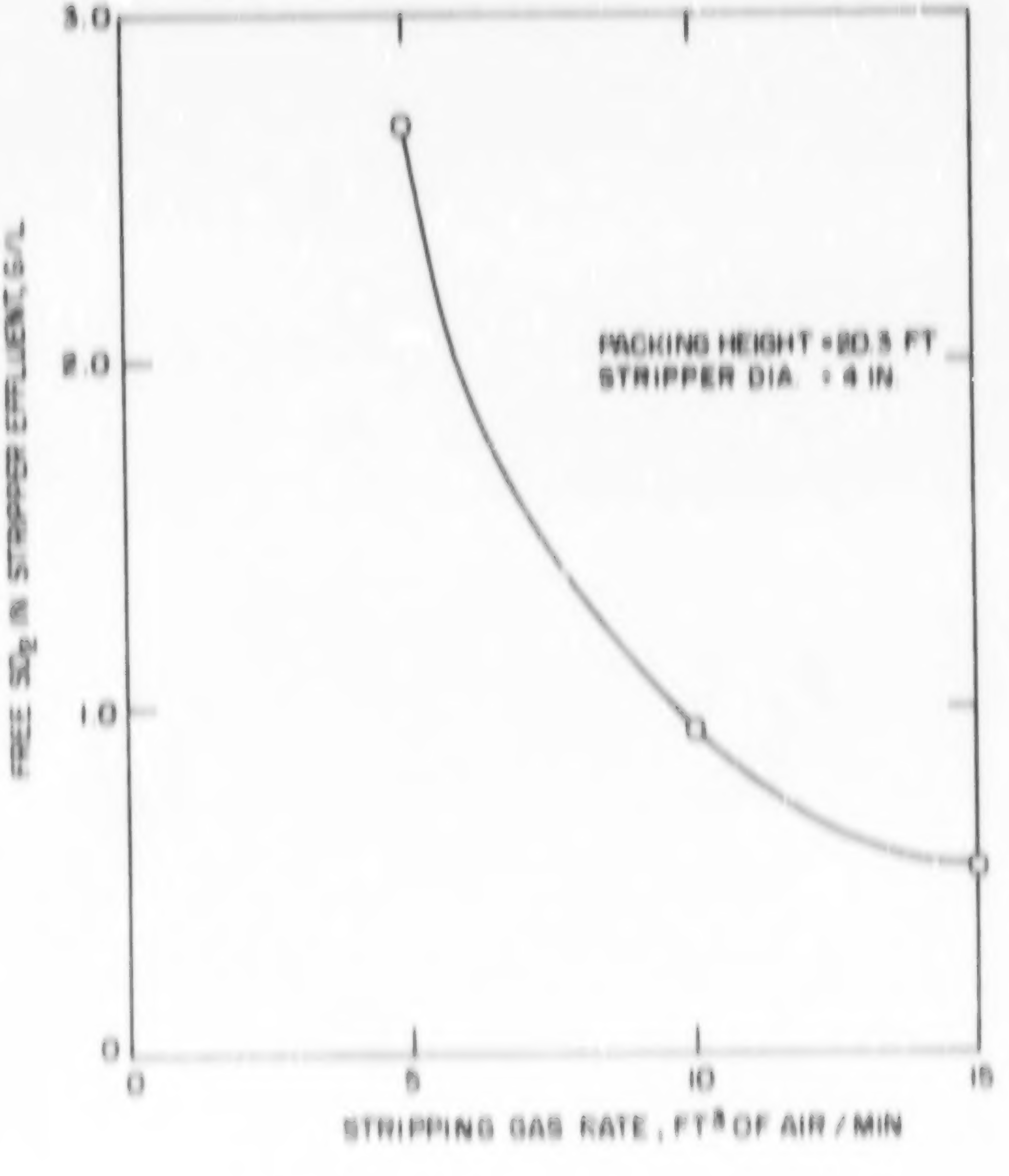


Figure 21: Effect of stripper gas rate on $SO_2$ in stripper effluent

## TABLE 5. TYPICAL REGENERATION TEST DATA

| | |
|---|---|
| Flowrates | |
| Product liquor, gpm | 0.45 |
| Sulfuric acid, gpm | 0.076 |
| Stripping gas (air), ft$^3$/min | 5.0 |
| Temperature, °F | |
| Product liquor | 123 |
| Sulfuric acid | 61 |
| Stripping gas | 61 |
| Stripper effluent | 89 |
| Stripper exit gas | 104 |
| Liquor analyses | |
| Product liquor to acidulator-stripper | |
| Sulfite sulfur, g/l | 30.76 |
| Bisulfite sulfur, g/l | 105.23 |
| Sulfate sulfur, g/l | 32.59 |
| Total sulfur, g/l | 168.58 |
| Specific gravity, g/ml | 1.242 |
| pH | 5.7 |
| Sulfuric acid, % $H_2SO_4$ | 91.4 |
| Stripper effluent | |
| Sulfite sulfur, g/l | 0.0 |
| Bisulfite sulfur, g/l | 0.0 |
| Sulfate sulfur, g/l | 100.46 |
| Bisulfate sulfur, g/l | 22.42 |
| Free $SO_2$, g/l | 0.12 |
| Total sulfur, g/l | 122.95 |
| Specific gravity, g/ml | 1.230 |
| pH | 1.7 |
| Acidulation stoichiometry[a] | 1.164 |
| Acidulation efficiency, % | 100 |
| Percent of released $SO_2$ that is stripped | 99.9 |
| Stripper packing height | 30 |

[a] Acidulation stoichiometry refers to the mol ratio of the acid ions from sulfuric acid to the ammonium ions (from ammonium sulfite and bisulfite) in the absorber product liquor.

effect unit was acceptable while operating at a temperature of 170°F and an absolute pressure of about 8 in. Hg (22 in. Hg vacuum). The 170°F limitation was set to minimize corrosion in the type 316L SS unit.

The concentrated $(NH_4)_2SO_4$ slurry from the evaporator-crystallizer was fed to a continuous belt filter. The filter (Eimco Model 112) had a 12-in.-wide belt with a total of 10 ft² filtering area. The unit proved to be greatly oversized for continuous operation, even at the lowest belt speed and with the $(NH_4)_2SO_4$ slurry entering the filter at the point that used the least amount of filtering area. Sufficient material could not be maintained on the belt to prevent vacuum breaks. In a batchwise operation, the filter system removed crystals sufficient to balance the pilot-plant production rate of 200 lb/hr.

Approximately 1,000 lb of crystals were removed on the belt filter. The crystals were sized about 70% plus 35 mesh and contained 5-10% moisture. The crystals were dried in a gas-fired rotary dryer to 2% or less moisture and bagged in standard fertilizer bags. The bags were left open and stored 9 mo in an open-air shed. The material was free-flowing at the end of the storage period.

Centrifuges are used in most commercial $(NH_4)_2SO_4$ production facilities. The belt filter was replaced with a 6-in. screen-bowl centrifuge manufactured by Bird Machinery Company. Slurry from the evaporator-crystallizer was pumped continuously to the centrifuge. A crystal separation rate of 200 lb/hr was achieved when the ammonium sulfate solids in the feed to the centrifuge was 10%. The moisture content of the cake was 3%. Line pluggage occurred when the solids content was 15%. When the solids content was decreased to 5%, the cake moisture content increased and eventually became "mud." Variation of the centrifugal force (760, 1,040, and 1,150 lb force/lb mass) had little or no effect on the cake moisture.

## Ammonium Sulfate Decomposer Design

EPA had the responsibility for developing the design of the decomposer to be used in the ammonium bisulfate study. Some work had been done by others on the decomposition step although none used solutions generated on power plant stack gases. In the 1920's a fertilizer process (22) was developed that required decomposition of $(NH_4)_2SO_4$ to drive off ammonia and produce ammonium bisulfate, which was then used as an acidulate to release $SO_2$. More recently, an engineering company (23) used the bisulfate process in various fertilizer flowsheets. However, the decomposition step has not been demonstrated in a continuous operation in any of these facilities. An objective of the Phase III work was to operate the complete absorption-regeneration system including an $(NH_4)_2SO_4$ decomposer. Dr. Richard M. Felder, Associate Professor of Chemical Engineering at North Carolina State University, was contracted (EPA purchase order No. 4-02-04510) to survey the literature and develop the necessary reaction kinetics and rate equations. These equations and data were used to design the reactor vessel with appropriate temperatures and reaction times. Felder's work covering the reaction kinetics and the engineering design basis for the reactor is included in this report as Appendix G. He recommended that the reactor be designed to operate at 700°F with a melt retention time (melt mass divided by feed rate) of 7.1 hr when using a steam to $(NH_4)_2SO_4$ mass ratio of 0.2. (The steam is necessary to sweep the released $NH_3$ from the melt and to prevent decomposition of $NH_4HSO_4$ to ammonium pyrosulfate and water.)

Ajax Electric Company, in Philadelphia, a manufacturer of molten salt bath furnaces, was contracted to furnish a workable design complete with detailed drawings that met the design criteria as specified by Felder. The Ajax contract was handled by Research Triangle Institute, Research Triangle Park, North Carolina (RTI contract No. 1006), as a part of Research Triangle Institute's service contract with EPA.

The decomposer design specified an inside dimension of 3 ft diameter by 6 ft high and had melt outlets at the 15- and 24-in. levels corresponding to retention times of 4 and 7 hr at the base feed rate of 300 lb/hr of ammonium sulfate.

The decomposer wall had a 9-in. thickness of acid-resistant brick plus 5 in. of insulating material. The outer shell was aluminized steel.

Heat input to the system was by current flowing through the electrically resistant melt. The power source was single-phase, 60-hertz, 460-V to the primary side of an 80-kW-rated transformer. The secondary voltage was infinitely variable from 30 to 50 V to maintain the desired temperature of the melt up to a maximum temperature of 750°F. Two 6-in. carbon electrodes carried current to and from the melt. Both the spacing and the immersion depth of the electrodes could be varied. The test program was to determine the effect of electrode spacing, electrode immersion depth, voltage and steam flow on one or more of the following response variables: power input, melt temperature, ammonium sulfate decomposition rate, electrode consumption, rate of formation of pyrosulfate, and ammonia concentration in the melt and vapor space.

The decomposer development program was stopped short of the construction phase because of unfavorable economics for a full-scale stack gas desulfurization process employing an electrical thermal decomposer.

## ECONOMIC EVALUATION

Cost estimates were made to permit comparison of the investment and net equivalent unit revenue requirements (mills/kWh) for the ammonium absorption - ammonium bisulfate regeneration (ABS) process with several advanced FGD processes. Each process was designed to desulfurize the flue gas from a 500-MW, new, coal-fired power plant unit burning coal with 3.5% S (dry basis). The study was based on 1975 costs and available technology. The results of the estimates are summarized in Table 6 and given in detail, including flowsheets, in Appendix H. Brief descriptions of the processes follow:

Process 1 is the ABS process as originally envisioned, in which the $SO_2$ is recovered from the ammoniacal absorber product liquor by acidulating with $NH_4HSO_4$ and stripping with air; it then is used in the production of sulfuric acid. Ammonia is evolved in the $(NH_4)_2SO_4$ decomposition step, recovered and recycled to the absorption step. It was assumed for this study that the absorber could be operated without a plume by control of operating conditions. This assumption may be proven with limited further experimentation. Should it not be verified, elimination of plume may be obtained through use of a wet electrostatic precipitator as an absorber and plume collector at some added cost, as described later.

Process 2 is a noncyclic adaptation of the ABS process in which the $SO_2$ in the absorber product liquor is recovered as $(NH_4)_2SO_4$. Since there is no regeneration section, $NH_3$ leaves the system as a part of the $(NH_4)_2SO_4$. Again it was assumed that the plant could be operated without a plume by control of operating conditions. Should this not be acceptable, an absorber-wet electrostatic precipitator could be used at added cost.

Process 3 is the basic limestone slurry absorption process with simple sludge throwaway. No salable or useful byproducts are redeemed in the process. It is recognized that fixation of sludge may be necessary to meet disposal requirements. Fixation would improve its compaction characteristics and result in longer disposal-pond life and better landfill capability.

Process 4 is a regeneration process that involves scrubbing with a slurry of magnesia to absorb the $SO_2$. The product stream of the absorbing slurry is dewatered, dried, and calcined. Magnesium oxide is regenerated and

TABLE 6. SUMMARY OF COSTS FOR VARIOUS FLUE GAS DESULFURIZATION PROCESSES[a]

| Process | Total capital investment, MM, $ | Gross annual revenue requirement, MM, $ | Net annual revenue requirement, MM, $ | Net unit revenue requirement, mills/kWh[b] |
|---|---|---|---|---|
| 1. Ammonia Absorption - Ammonium Bisulfate Regeneration - Sulfuric Acid Production[c] | 42.1 | 16.0 | 12.2 | 3.42 |
| 2. Ammonia Absorption Scrubbing Liquor Saturated with Ammonium Sulfate - Ammonium Sulfate Production | 32.5 | 16.6 | 10.0 | 2.87 |
| 3. Limestone Slurry Absorption - Ponding of Sludge (Throwaway) | 30.7 | 10.4 | 10.4 | 2.97 |
| 4. Magnesia Slurry Absorption - Sulfuric Acid Production[c] | 32.1 | 11.9 | 8.5 | 2.43 |
| 5. Sodium Sulfite Absorption - Sulfuric Acid Production[c] | 37.1 | 14.5 | 11.8 | 3.37 |

a. Basis:
500-MW new coal-fired power unit, 90% $SO_2$ removal.
Coal burned, 1,312,500 tons/yr, 3.5% S (dry basis), 9,000 Btu/kWh.
Stack gas reheat to 175°F by indirect steam reheat, entrained water 0.5% by wt (wet basis).
Power unit on-stream time, 7000 hr/yr.
Midwest plant location, 1975 revenue requirements.
Investment and revenue requirements for disposal of flyash excluded.
Remaining life of power plant, 30 yr.

b. Includes revenue from sale of byproduct: $30/ton 100% sulfuric acid; $44/ton ammonium sulfate; $24/ton sodium sulfate.

c. Regeneration process.

recycled to the absorption step, and $SO_2$ is evolved and is used in the production of sulfuric acid.

Process 5, also a regeneration process, uses a solution of sodium salts and makeup sodium carbonate ($Na_2CO_3$) to absorb the $SO_2$. Sodium sulfate ($Na_2SO_4$), resulting from oxidation in the absorber, is purged from the absorber product solution, crystallized and sold. The remaining sodium bisulfite ($NaHSO_3$) solution is evaporated and the resultant crystals thermally decomposed to give sodium sulfite ($Na_2SO_3$) and gaseous $SO_2$. The $Na_2SO_3$ is recycled to the absorption step and the $SO_2$ is used in the production of sulfuric acid.

As shown in the cost tabulation, the ABS process has the highest capital costs, $42.1 million, and the highest net unit revenue requirement, 3.42 mills/kWh. (Use of a wet electrostatic precipitator would increase these costs by 18% and 4% respectively.)

Process 2, ammonia absorption of $SO_2$ with $(NH_4)_2SO_4$ production has a capital requirement of $31.5 million and a net unit revenue requirement of 2.87 mills/kWh. (Use of an absorber-precipitator system would increase these costs by about 20% and 5% respectively.)

The limestone slurry process with ponding (throwaway) of sludge (Process 1) has an estimated capital requirement of $30.7 million and a unit revenue requirement of 2.97 mills/kWh. If sludge fixation is necessary, the unit revenue requirement will increase by about 17%.

The magnesia slurry process (No. 4), which produces sulfuric acid, has the lowest unit revenue requirement, 2.68 mills/kWh, and one of the lowest capital requirements $32.3 million.

The sodium sulfite process with production of sulfuric acid was indicated to be more costly than the magnesia process; capital requirement is $37.1 million and net unit revenue requirement is 3.19 mills/kWh.

A study, sponsored by EPA, investigated the economics of using $(NH_4)_2SO_4$ from an ammonia scrubbing FGD process as a replacement for anhydrous $NH_3$ for direct application of nitrogen to the soil. It was assumed that the ammonia planned for direct application would be routed to the power plant, used for absorbing $SO_2$ from the flue gas, and recovered as $(NH_4)_2SO_4$, which then would be transported and applied to the soil as a replacement for anhydrous $NH_3$.

Two midwestern coal-fired power plants were chosen for the study. The first, in Kincaid, Illinois, is in an area of high-density agricultural $NH_3$ consumption. The power plant at Kincaid is rated at 1,300 MW and has the potential to produce 402,396 tons of $(NH_4)_2SO_4$ annually at a rate of 1,219 tons/day. The second plant is at Paradise, Kentucky, a region of low-density agricultural $NH_3$ consumption. The plant is rated at 2,450 MW and has the potential to produce 961,251 tons of $(NH_4)_2SO_4$ annually at a rate of 2,913 tons/day.

The results of this study indicated that the sum of the costs of handling, transporting, storing, and applying a ton of $NH_3$ to the soil as $(NH_4)_2SO_4$ may be about $28 less than that for $NH_3$ as anhydrous $NH_3$ in the high-use area (Kincaid, Illinois) and about $8 less in the low-use area (Paradise, Kentucky). The cost of FGD is not included.

# CONCLUSIONS AND RECOMMENDATIONS

## CONCLUSIONS

Phase I of the pilot-plant study demonstrated that ammonia absorption as applied to $SO_2$ removal from coal-fired power plants was effective (90% or higher) over a wide range of operating conditions. Specific conclusions from the Phase I work were:

1. The absorption efficiency can be reliably predicted for given operating parameters.
2. Ammonium sulfate levels in the absorber loop have only slight influence on $SO_2$ absorption.
3. Flyash has a negligible effect on $SO_2$ removal.
4. Temperature of the inlet flue gas has little effect on $SO_2$ removal in the range covered by the study (180-300°F).
5. Corrosion was not a problem in the absorption loop when using SS and certain nonmetals.

The favorable results from the Phase I study led to the recommended decision to expand the work to include a study of a regeneration scheme to make the process cyclic. This work, called Phase II, began the investigation of the ammonium bisulfate process for recovery of ammonia to be used in regenerating the ammoniacal liquor from the absorber section. The conclusions drawn from the Phase II study were:

1. The plume identified and only casually examined in the Phase I work is persistent, and precise control of the absorber operation is required in order to meet an opacity limit of 5% in the pilot plant (about 20% in commercial stack). Equipment modifications were made in the Phase III work in an effort to obtain the necessary precise control of the absorber operation.
2. Formation of a plume is less likely to occur at low liquor concentrations ($C_A < 1$) than at higher concentrations ($C_A = 12$).

3. Reheat is required to dissipate the steam plume from the absorber. Under certain ambient conditions (temperature and humidity) dissipation of the steam plume by reheat is either impossible or impractical.

4. Regeneration of the absorber liquor by acidification and stripping removes and recovers up to 99% of the absorbed $SO_2$.

5. Corrosion in the regeneration loop requires use of low-carbon SS and plastics.

Though difficulties were identified (for instance, separation of flyash and ammonium sulfate crystals from liquors in the system) they did not appear to be technically insurmountable. A recommendation was then made to extend the work into Phase III to study the complete, closed-loop regeneration system.

The plume problem was not overcome in the third phase of the pilot-plant study. Also, the economics of the process were unfavorable. Conclusions drawn from the work are:

1. Absorption was adequate (90% or higher) using scrubbing liquors of moderate-to-high salt concentration ($C_A$ = 10-15).

2. While operating at these liquor concentrations, effective and consistent plume control (pilot-plant stack opacity 5% or less) was not achieved by methods and equipment tested in the pilot plant.

3. An in-line indirect steam-heated reheater dissipated the water vapor in the scrubbed flue gas but did not significantly reduce the opacity of the ammonia-sulfur compound plume.

4. Bench-scale studies identified chloride and $SO_3$ (both found in the inlet flue gas) as fuming agents.

5. Predictions of the formation of the ammonia-sulfur fume, presumably ammonium sulfite monohydrate, can be made from a thermodynamic equation derived from the equilibrium constant for the reaction:

$$2NH_3 + 2H_2O + SO_2 \rightarrow (NH_4)_2SO_3 \cdot H_2O$$

This study indicated that the fume prediction equations must be satisfied as a necessary, but not limiting, condition for fumeless operation; for instance, chlorides and $SO_3$ are not considered in the equation.

6. Essentially complete acidulation of the absorber product liquor was accomplished using sulfuric acid.

7. The stripper removed 99.9% of the free $SO_2$ from the acidulated absorber product liquor. The liquor effluent from the stripper ammonium sulfate solution was essentially free of $SO_2$.

8. The combined off-gas stream from the acidulator and stripper contained approximately 60% $SO_2$, which is more than adequate for a feed gas stream to an $H_2SO_4$ plant.

9. The evaporator-crystallizer produces an ammonium sulfate slurry suitable for separation of crystalline ammonium sulfate.

10. Standard ammonium sulfate separation techniques appear to be acceptable for removing crystalline ammonium sulfate from the evaporator-crystallizer slurry.

11. A comparative economics study of the $NH_3$-ABS process and other more advanced regenerable and nonregenerable processes (500-MW units) showed that the $NH_3$-ABS process had the highest fixed investment cost and next to the highest annual revenue requirement (operating costs).

## RECOMMENDATIONS

1. Developmental work on the $NH_3$-ABS process should cease. The prime drawbacks to the process are the plume problem and the unfavorable economics. Attempts to control the fume have met with little success. The ABS process is a high energy-consuming process. The electrical thermal decomposer in the regeneration section requires nearly 50% of the power requirement for the entire FGD system (see Table H-1A). The cost of power, which has more than doubled since the study began, is the major factor in forcing the ammonium bisulfate process into an unfavorable economic situation. Calculations based on information obtained from vendors indicate that use of wet electrostatic precipitators to collect the fume would add about 15% to the capital cost of the ABS system, further adding to its already untenable economic position.

2. The emphasis of any further ammonia absorption pilot-plant work should be directed toward a nonregenerable process to eliminate the costly decomposition step.

The ammonia absorption system can produce $(NH_4)_2SO_4$, a nitrogen source in the formulation of some fertilizers. Indications are that $(NH_4)_2SO_4$ produced during $SO_2$ absorption can be sold as a fertilizer at a price high enough to recover the cost of ammonia. A comparative economics study showed that a system to produce $(NH_4)_2SO_4$ during $SO_2$ removal has a much lower unit revenue requirement than does the ABS process. The study also showed that the ammonia absorption - $(NH_4)_2SO_4$ process is at least as attractive economically as the limestone slurry process with simple sludge throwaway (2.87 and 2.97 mills/kWh respectively). Even with a mechanical or electrical particulate collector added to the system, it remains competitive. A marketing study showed that the cost of handling and applying ammonia to the soil as ammonium sulfate is competitive with applying the ammonia as anhydrous ammonia.

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# APPENDIX A

# ANALYTICAL AND GAS SAMPLING PROCEDURES

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# APPENDIX A

# ANALYTICAL AND GAS SAMPLING PROCEDURES

## IODIMETRIC METHOD FOR ANALYSIS OF TOTAL SULFITES

### Manipulations

Aliquot 25 ml of the scrubber solution into a 1,000-ml volumetric flask containing about 300 ml of condensate water. Use caution to see that the discharge end of the pipette is under the water. Dilute to volume. In a 250-ml wide-mouth erlenmeyer flask add 10 ml of 1-10 HCl and 35 ml of 0.1 N $I_2$ (more may be used if necessary). Aliquot 20 ml of the diluted sample under the surface of the iodine. Allow time to react and back titrate the excess $I_2$ with 0.1 N $Na_2S_2O_3$.

### Calculations

g/l total sulfites =

$$\frac{\text{ml } I_2 - (\text{ml } Na_2S_2O_3 \times N\ Na_2S_2O_3/N\ I_2) \times N\ I_2 \times 0.0160328 \times 1000}{\text{ml sample analyzed}} =$$

## ALKIMETRIC METHOD FOR ANALYSIS OF TOTAL BISULFITE SULFUR AND TOTAL SULFUR

### Manipulations

Aliquot 10 ml of sample to a 250-ml volumetric flask containing about 100 ml of deionized water and 10 ml of 30% hydrogen peroxide. Make to volume with deionized water and allow to cool and make to volume again, mix thoroughly.

Take a 20-ml aliquot of the diluted sample into a 250-ml, wide-mouth erlenmeyer flask. Add 8 drops of methyl red-methylene blue mixed indicator to the flask. Titrate with approximately 0.2 N NaOH to the first green end point. Record the ml of NaOH used as the titer Ta for calculating the grams per liter of bisulfite sulfur.

Add 10 ml of formaldehyde to the same sample. Add one dropper of phenolphthalein-methylene green indicator, continue to titrate with the 0.2 N NaOH through the blue color, through the green color, and to the first dark blue color. Record the ml of NaOH used; this is titer Tb.

Establish a blank on each new bottle of formaldehyde. Add 20 ml of deionized water to a 250-ml erlenmeyer flask, add 10 ml of formaldehyde to the flask, add eight drops of methyl red-methelene blue indicator. Titrate to the green end point with 0.2 N NaOH. The ml of the 0.2 N NaOH used to titrate 10 ml of formaldehyde is the blank.

Calculations

$$\text{g/l } HSO_4 = \frac{\text{ml NaOH (Ta)} \times \text{N NaOH} \times 0.032064 \times 1000}{\text{ml of sample analyzed}}$$

$$\text{g/l total sulfur} = \frac{(\text{Tb} - \text{blank}) \times \text{N NaOH} \times 0.0160328 \times 1000}{\text{ml of sample analyzed}}$$

## ANALYSIS OF THE ACIDULATOR AND STRIPPER LIQUORS FOR BISULFITE, BISULFATE, AND TOTAL SULFUR

The total sulfites are determined by the iodimetric method. It is assumed that when the pH of the acidulator is 2.0 or below, that all of the sulfites are in the form of ammonium bisulfite. The acidulator and stripper also contain ammonium bisulfate and ammonium sulfate. The acidulator and stripper are analyzed essentially the same way as the samples from the ammonium scrubber pilot plant, as described above; however, the calculations are somewhat different.

The total sulfites are calculated to ammonium bisulfites. A separate determination is made for the ammonium bisulfate and total sulfur alkimetrically.

Manipulations

Aliquot 10 ml of the sample into a 250-ml volumetric flask containing about 100 ml of deionized water and 10 ml of 30% hydrogen peroxide; make to volume with deionized water. Take a 20-ml aliquot into a 250-ml erlenmeyer flask. Add to it 10 drops of methyl red-methylene blue mixed indicator. Titrate with 0.2 N NaOH to the green end point, and record ml used as the titer Ta for calculating the ammonium bisulfate. Add 10 ml of formaldehyde to the sample, then one dropper of phenolphthalein-methylene green mixed indicator, continue to titrate through the blue color, through the green color, and to a dark blue color. This is the end point for the total sulfur, record mls used as titer Tb.

Establish a blank on each new bottle of formaldehyde. Add 20 ml of deionized water to a 250-ml erlenmeyer flask, add 10 ml of formaldehyde to the flask, add eight drops of methyl red-methylene blue indicator. Titrate to the green end point with 0.2 N NaOH. The ml of 0.2 N NaOH used to titrate 10 ml of formaldehyde is the blank.

## Calculations

Ammonium Bisulfate--

$$\text{g/l}\ \frac{(\text{NH}_4\text{HSO}_4)(\text{ml sample})}{N\ \text{NaOH} \times 99.112} = \text{ml } 0.2\ N\ \text{NaOH due to NH}_4\text{HSO}_4 = a$$

$$\text{g/l NH}_4\text{HSO}_4 = \frac{(Ta-a) \times N\ \text{NaOH} \times 115.112}{\text{ml sample analyzed}}$$

Total Sulfur--

$$\text{g/l total sulfur} = \frac{(Tb - \text{blank}) \times N\ \text{NaOH} \times 16.0329}{\text{ml sample analyzed}}$$

## SILVER NITRATE METHOD FOR ANALYSIS OF CHLORIDE

The pH of the sample to be tested is adjusted between the limits indicated by methyl orange and phenolphthalien indicators. The chloride ion is titrated with silver nitrate solution in the presence of potassium chromate. The silver reacts with the chloride forming silver chloride which precipitates. When all the chloride has precipitated, red silver chromate is formed thus indicating the end point.

## Manipulations

The sample to be tested should have been previously filtered through Whatman No. 42 filter paper or similar grade paper. From previous analysis, estimated concentration, and the tabulation below determine size sample to analyze. The concentration of chloride ion should be between 5 and 200 ppm in the portion titrated.

| Estimated ppm chloride | Sample size, ml |
|---|---|
| 5-150 | 100 |
| 150-300 | 50 |
| 300-650 | 25 |
| Above 650 | 10 |

Pipet size sample selected into a porcelain casserole. When size sample selected is less than 100 ml, dilute the sample to about 100 ml with distilled water. Add a few drops of 0.1% phenolphthalein indicator to the sample and discharge the pink color by careful addition of a few drops of 0.5 N sulfuric acid[a]. Add about 1 ml of potassium chromate solution to the sample. Titrate the sample with standard silver nitrate until one drop produces a faint reddish color that does not disappear upon stirring. Record the ml of silver nitrate as titer Ta. Using reagents used in the analyses, make a blank determination by titrating a volume of distilled water equal to that used to dilute sample.

Calculations

$$Cl^{-} mg/l = \frac{[ml\ AgNO_3\ (Ta) - blank]\ x\ (mgCl^{-}/ml\ silver\ nitrate)\ x\ 1000}{ml\ analysed}$$

AMMONIA IN EXIT FLUE GAS SAMPLE (DIRECT NESSLERIZATION METHOD)

Method

Nessler reagent and Rochelle salt solution are added to the sample to be tested. The resulting color intensity is determined with a spectrophotometer by taking the light transmittance at 425 millimicrons through a 2.5-cm cell.

The $NH_3$ concentration in the unknown sample is determined by comparing its color intensity with the color intensities of samples containing known concentration of $NH_3$. The comparison is made from a graph previously prepared by plotting the light transmitted through the color developed in standard samples against the concentration of ammonia in them.

Manipulations

1. From previous analyses of the same type samples, estimate the concentration of $NH_3$ in the sample. Then use the tabulation below to determine aliquot to use.

---

[a] If for any reason the sample of water is acid, add 0.5 N sodium hydroxide solution until a pink color is obtained with phenolphthalein solution. Then add just enough 0.5 N sulfuric acid to discharge the pink color.

Sample concentration, dilution, and aliquot to use

| Approximate concentration, ppm $NH_3$ | ml of original taken | Volume diluted to, ml | ml of diluted sample analyzed | ml original analyzed |
|---|---|---|---|---|
| 0.0-1.4 | - | - | - | 100 |
| 1.5-2.9 | - | - | - | 50 |
| 3.0-7.3 | - | - | - | 20 |
| 7.4-14.5 | 50 | 500 | 100 | 10 |
| 14.5-29.0 | 25 | 500 | 100 | 5 |
| 29.0-58.1 | 25 | 500 | 50 | 2.5 |

2. Transfer selected aliquot of filtered samples into separate 100-ml Nessler tubes. If aliquot is less than 100 ml, dilute to 100 ml with ammonia-free distilled water. Always test distilled water for ammonia before using it. If sample is colored or turbid and not water clear, transfer a duplicate aliquot into another Nessler tube. Add 1 ml of Rochelle salt and determine light transmitted through it to make sure it is not darker than reagent blank used to adjust instrument as described below. If its color is darker than reagent blank, adjust instrument with it and determine light transmitted through portion of same sample reacted with Nessler at the new instrument setting.

3. Prepare a reagent blank by adding 100 ml of ammonia-free distilled water to another 100-ml Nessler tube.

4. Add 1 ml of Rochelle salt solution to each sample and reagent blank. Stopper each Nessler tube with clean polyethylene stopper and mix by inverting two or three times. Never use rubber stoppers in this step and step 5 because a color other than ammonia reaction may result.

5. Add 1 ml of Nessler reagent solution to each sample and reagent blank; again, stopper and mix as in step 4. Allow color to develop 30 minutes.

6. Transfer sample containing Rochelle salt and Nessler reagent into spectrophotometer test tube and read percent transmittance.

7. From transmittance reading determine mg $NH_3$ and/or ppm from a prepared chart.

Calculations

$$\frac{\text{mg } NH_4 \times 1000}{\text{ml of orig. sample used for comparison}} = \text{ppm } NH_4$$

ppm $NH_4$ x 0.944 = ppm $NH_3$

ppm $NH_4$ x 0.777 = ppm N

## PREPARATION OF AMMONIA REAGENTS (FOR NESSLER METHOD)

### Nessler Reagent

Dissolve 100 g mercuric iodide ($HgI_2$) and 70 g potassium iodide, (KI) in a small quantity of ammonia-free distilled water and add this mixture slowly, with stirring, to a cool solution of 160 g NaOH in 500-ml ammonia-free distilled water. Dilute to 1 liter with ammonia-free distilled water.

Stored in Pyrex glassware and out of sunlight, this reagent is stable for periods up to a year under normal laboratory conditions.

The reagent should give the characteristic color with mg/l ammonia nitrogen within 10 min after addition but should not produce a precipitate with small amounts of ammonia within 2 hr.

CAUTION: This reagent is very toxic; take care to avoid ingestion.

### Rochelle Salt Reagent

Dissolve 500 g of reagert grade $KNaC_4H_4O_6 \cdot 4H_2O$ in 1 liter of distilled water. Boil off 200 ml or until free from ammonia. Cool and dilute to 1 liter with ammonia-free distilled water.

## PREPARATION OF STANDARD AMMONIUM CHLORIDE AND AMMONIUM SULFATE SOLUTIONS FOR CALIBRATING SPECTROPHOTOMETERS

### Ammonium Chloride and Ammonium Sulfate Stock Solutions

Dissolve 1.1862 g anhydrous reagent grade ammonium chloride or 1.4652 g ammonium sulfate, dried at 100°C, in ammonia-free distilled water and dilute to 2000 ml with $NH_3$ free distilled water. Mix well.

### Standard Solution Containing 0.002 mg $NH_3$ per ml

Pipet 20 ml of either stock solution and transfer into a 2000 ml volumetric flask. Dilute to 2000 ml with ammonia-free distilled water and mix well. This solution is used for calibrating spectrophotometers.

## PROCEDURE FOR SAMPLING INLET OR EXIT FLUE GAS FOR PARTICULATE AND SULFUR DIOXIDE

### Sampling

Apparatus (Figure A-1)--

- A. Environeering dust filter.
- B. Four 600-ml gas scrubber bottles arranged in order listed below. (An additional scrubber bottle of peroxide may be required for inlet determinations.)
    1. Dry trap with short open-end sparger.
    2. 6% hydrogen peroxide solution with fritted glass impinger (250 ml).
    3. 6% hydrogen peroxide solution with fritted glass impinger (250 ml).
    4. Dry trap with short open-end sparger.
- C. Dry test meter.
- D. Vacuum supply.

Procedure --

- A. Insert Environeering sample nozzle into gas duct.
- B. Pull approximately 0.5 cfm sample for about 120 min (increase vacuum to maintain flow).
- C. Record pressure and temperature readings at meter.
- D. Record pressure and temperature readings of duct (wet and dry bulb for exit gas sample).
- E. Combine the peroxide bottles and analyze for $SO_2$.
- F. Dry the filter paper at 110°F and weigh.

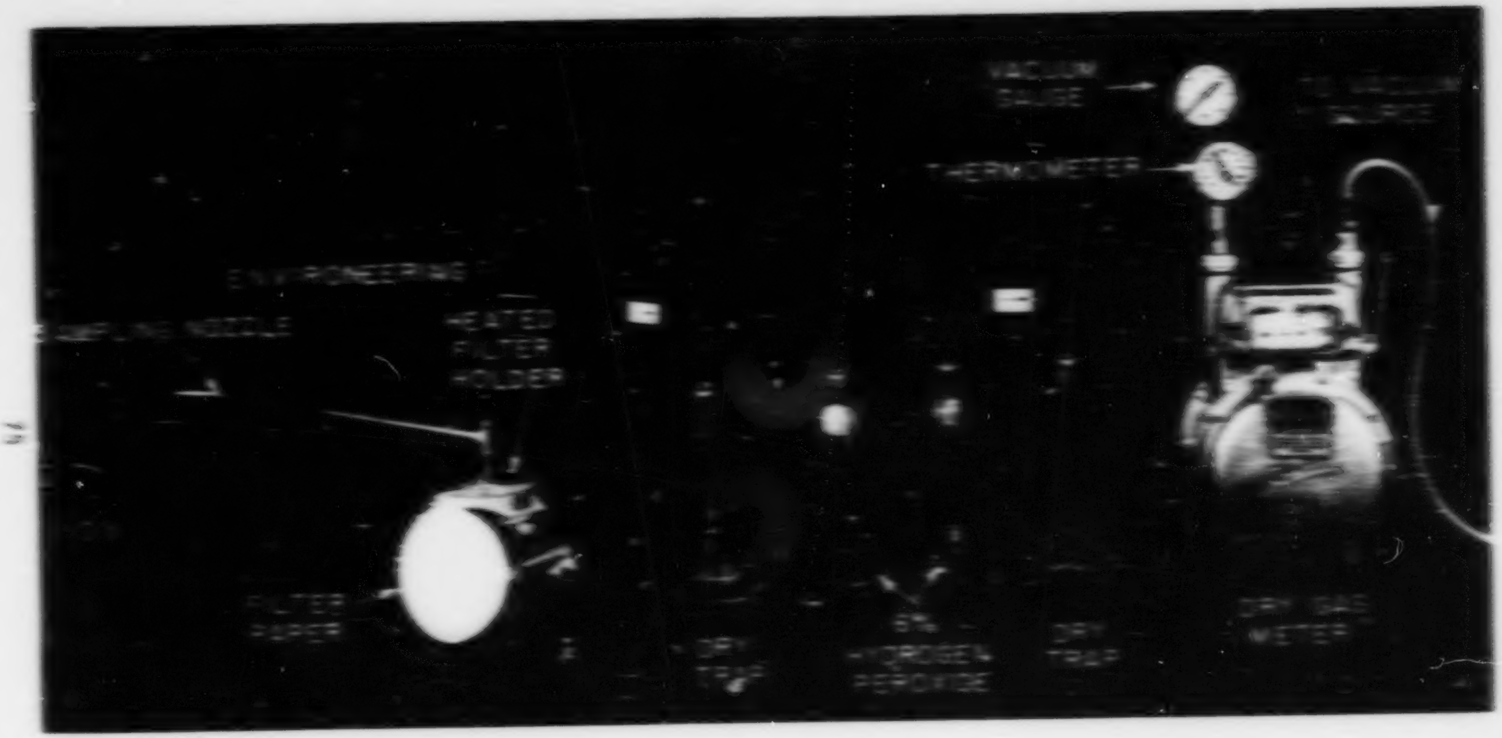
VACUUM GAUGE
TO VACUUM SOURCE
THERMOMETER
ENVIRONEERING
SAMPLING NOZZLE
HEATED FILTER HOLDER
FILTER PAPER
DRY TRAP
6% HYDROGEN PEROXIDE
DRY TRAP
DRY GAS METER

Figure A-1. Gas sampling apparatus for $SO_2$ and particulate.

## Sample Calculation Sheet

Particulate and Sulfur Dioxide in Inlet Flue Gas--

### Test Data--

| | |
|---|---|
| Dry test meter readings | |
| Total volume through meter, ft³ | 23.2 |
| Temperature of meter, °F | 58 |
| Vacuum on meter, in Hg | 7 |
| Sampling time, min | 60 |
| Dust collected during sampling period, g | 5.3320 |
| Sulfur caught in peroxide during sampling period, g | 1.89 |
| Average moisture of inlet gas during sampling period, % | 7.75 |

### Calculations--

1. To convert the volume at meter conditions to the volume at standard conditions, use the pressure-volume-temperature relationship expressed in the ideal gas law.

$$\frac{P_o V_o}{T_o} = \frac{P_1 V_1}{T_1}$$

where

$P_o$ = initial pressure, in Hg
$V_o$ = initial volume, ft³
$T_o$ = initial temperature, °R or (460 + °F)

and $P_1$, $V_1$, and $T_1$ = above values at standard conditions

Transposing,

$$V_1 = \frac{P_o V_o T_1}{T_o P_1}$$

Inserting test data values,

$$V_1 = \frac{(29.92 - 7.0)^a (23.2)(460 + 70)}{(460 + 58)\ (29.92)}$$

$$= \frac{(22.92)(23.2)\ 530}{(518)(29.92)}$$

$$= 18.18 \text{ ft}^3$$

---

a. Vacuum on meter.

Converting from wet volume to dry volume, use the formula

$$V_{dry} = V_{wet} \frac{(100 - \text{avg \% moisture by volume})}{100}$$

$$= (18.18)\ \frac{(100 - 7.75)}{100}$$

$$= (18.18)\ (0.9225)$$

$$= 16.78\ \text{ft}^3\ \text{(dry at 29.92 in Hg and 70°F)}$$

2. To convert the weight of dust collected on the filter during the sampling period into dust concentration in $gr/dscf_{70}$, merely convert the weight in g to gr by multiplying by 15.43 (the number of gr in 1 g) and divide by the dry volume of gas at standard conditions.

$$\text{Dust loading} = \frac{(5.3320)\ (15.43)}{16.78}$$

$$= 4.9030\ gr/dscf_{70}$$

3. To convert the weight of sulfur caught in the peroxide bottles into its equivalent volume of $SO_2$, divide the weight of the sample by the gram molecular weight of sulfur and multiply the quotient by the mol volume (in liters) divided by 28.32 (the number of liters in 1 ft³).

$$\text{Vol. } SO_2 \text{ sampled} = \frac{\text{sample weight}}{\text{g mol wt of S}} \times \frac{22.4}{28.32}$$

$$= \frac{1.89}{32.06} \times 0.791$$

$$= 0.04664$$

To convert the volume of $SO_2$ sampled to ppm in inlet gas, multiply the volume by $10^6$ and divide by the combined volume of $SO_2$ plus inlet gas.

$$SO_2 \text{ in inlet gas} = \frac{\text{vol of } SO_2 \text{ sampled} \times 10^6}{\text{vol of } SO_2 \text{ sampled} + \text{vol of gas}}$$

$$= \frac{0.04664 \times 10^6}{0.04664 + 16.78}$$

$$= 2772\ \text{ppm}$$

Particulate and $SO_2$ in Exit Flue Gas--

Test Data--

| | |
|---|---|
| Dry Test meter readings | |
| Total volume through meter, ft$^3$ | 17.8 |
| Temperature of meter, °F | 58 |
| Vacuum on meter, in Hg | 7 |
| Sampling time, min | 60 |
| Wet-bulb temp. exit scrubber, °F | 105 |
| Dry-bulb temp. exit scrubber, °F | 106 |
| Dust collected during sampling, g | 0.005 |
| Sulfur caught in peroxide during sampling, g | 0.33 |

Calculations--

1. To convert the volume of gas from meter conditions to dry standard cubic feet at atmospheric pressure and 70°F, use the formulas below.

$$V_1 = \frac{(29.92 - 7)(17.8)(460 + 70)}{(460 + 58)(29.92)}$$

$$= 13.95$$

$$V_{dry} = V_{wet}\ \frac{(100 - \text{avg \% moisture by volume})}{100}$$

$$= \frac{13.95\ (100 - 7.9)}{100}$$

$$= 12.86\ (\text{dscf}_1)$$

2. From the psychrometric chart, gas with a wet-bulb temperature of 105°F and a dry-bulb temperature of 106°F contains 0.0508 lb of water per lb of dry air.

Then

$$\text{\% moisture by volume} = \frac{\left(\frac{\text{lb } H_2O/\text{lb dry air}}{18}\right) \times 100}{\left(\frac{\text{lb } H_2O/\text{lb dry air}}{18} + \frac{1}{30.4}\right)}$$

where 30.4 is the average molecular weight of the flue gas.

$$= \frac{(0.00282) \times 100}{(0.00282 + 0.0329)}$$

$$= 7.9\%$$

3. To calculate the dust loading use the formula

$$\text{Dust loading, gr/dscf}_{70} = \frac{\text{g collected} \times 15.43}{\text{Vol of gas, dscf}_{70}}$$

$$= \frac{0.005 \times 15.43}{12.86}$$

$$= 0.0060 \text{ gr/dscf}_{70}$$

4. To convert the weight of sulfur caught in the peroxide bottles into its equivalent volume of $SO_2$, divide the weight of the sulfur by the gram molecular weight of sulfur and multiply the quotient by the mol volume (in liters) divided by 28.32 (the number of liters per ft$^3$).

$$\text{Vol } SO_2 \text{ sampled} = \frac{\text{sample wt}}{\text{g mol wt of S}} \times \frac{22.4}{28.32}$$

$$= \frac{0.33}{32.06} \times 0.791$$

$$= 0.008142$$

To convert the volume of $SO_2$ sampled to ppm in the exit gas, multiply the volume by $10^6$ and divide by the combined volume of $SO_2$ plus exit gas.

$$SO_2 \text{ in exit gas} = \frac{0.008142}{0.008142 + 12.86}$$

$$= 633 \text{ ppm}$$

## PROCEDURE FOR SAMPLING EXIT FLUE GAS FOR AMMONIA

### Sampling

Apparatus (see Figure A-2)--

A. Stainless steel sampling nozzle.
B. Four 600-ml gas scrubber bottles arranged in order listed below.
   1. Dry trap with short open-end sparger.
   2. Distilled water with fritted glass impinger (250 ml).
   3. Distilled water with fritted glass impinger (250 ml).
   4. Dry trap with short open-end sparger.
C. Dry test meter.
D. Vacuum supply.

Procedure--

A. Insert sampling nozzle into gas duct.
B. Pull approximately 0.5 cfm sample for about 30 min (increase vacuum to maintain flow).
C. Record pressure and temperature readings at meter.
D. Record pressure and temperature readings of duct (wet and dry bulb).
E. Combine the water bottles and analyze for $NH_3$ (see analysis procedure).

### Sample Calculation Sheet

Ammonia in Exit Flue Gas--

Test Data--

| | |
|---|---|
| Dry test meter readings | |
| Total volume through meter, $ft^3$ | 7.0 |
| Temperature of meter, °F | 58.0 |
| Vacuum on meter, in Hg | 3.0 |
| Sampling time, min | 60 |
| Wet-bulb temp. exit scrubber, °F | 105 |
| Dry-bulb temp. exit scrubber, °F | 106 |
| $NH_3$ caught in water during sampling, g | 0.01037 |

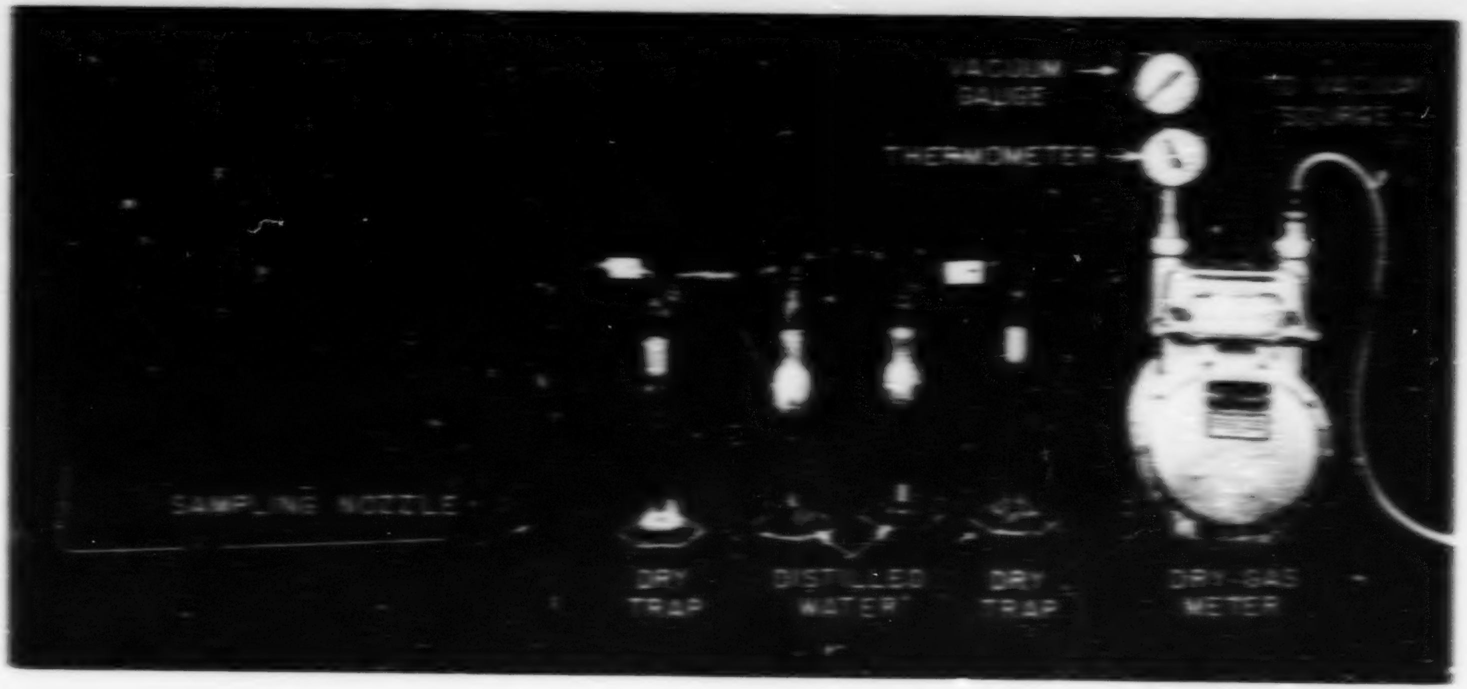
VACUUM GAUGE
TO VACUUM SOURCE
THERMOMETER
SAMPLING NOZZLE
DRY TRAP
DISTILLED WATER
DRY TRAP
DRY-GAS METER

Figure A-2. Gas sampling apparatus for ammonia.

## Calculations--

1. To convert the volume of gas from meter conditions to dry standard cubic feet at atmospheric pressure and 70°F, use the formulas below.

$$V_1 = \frac{(29.92 - 1.0)(7.0)(460 + 70)}{(460 + 58)(29.92)}$$

$$= 6.44 \text{ ft}^3 \text{ at } 70°\text{F}$$

2. From the psychrometric chart, gas with a wet-bulb temperature of 105°F and a dry-bulb temperature of 106°F contains 0.0508 lb of water per lb of dry air. Then

$$\% \text{ moisture by volume} = \frac{\left(\frac{\text{lb } H_2O/\text{lb dry air}}{18}\right) \times 100}{\left(\frac{\text{lb } H_2O/\text{lb dry air}}{18} + \frac{1}{30.4}\right)}$$

$$= \frac{(0.00282) \times 100}{(0.00282 + 0.0329)}$$

$$= 7.9\%$$

3. $$V_{dry} = V_{wet} \frac{(100 - \% \text{ moisture})}{100}$$

$$= 6.44 \frac{(92.1)}{100}$$

$$= 5.92 \text{ dscf}_{70}$$

To convert the weight of ammonia caught in the sample into its equivalent volume, divide the weight by the gram molecular weight of ammonia and multiply the quotient by the mol volume (22.4 l) divided by the liters per ft³ (28.32).

$$\text{Vol } NH_3 = \frac{0.01037}{18} \times \frac{22.4}{28.32}$$

$$= 0.000459 \text{ ft}^3$$

To convert this volume to ppm in the exit gas, multiply the volume by $10^6$ and divide by the combined volume of $NH_3$ plus exit gas.

$$\text{ppm } NH_3 = \frac{0.000459 \times 10^6}{0.000459 + 6.44}$$

$$= 71 \text{ ppm}$$

# APPENDIX B

## SAMPLE CALCULATIONS

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# APPENDIX B

# SAMPLE CALCULATIONS

## TYPICAL ABSORBER PRODUCT LIQUOR COMPOSITION

### Solution

| | | |
|---|---|---|
| Sulfite sulfur ($SO_3$ as S) | | 33.83 g/l |
| Bisulfite sulfur ($HSO_3$ as S) | | 109.18 g/l |
| Sulfate sulfur ($SO_4$ as S) | | 20.18 g/l |
| | Total | 163.19 g/l |

pH = 5.7
Specific gravity = 1.276

### Mols of Sulfur per Liter

Grams sulfur/l/molecular weight of sulfur = mols of sulfur/l
Sulfite sulfur = 33.83/32 = 1.06 mols/l
Bisulfite sulfur = 109.18/32 = 3.41 mols/l
Sulfate sulfur = 20.18/32 = 0.63 mols/l

### Total Grams of Salt per Liter

Mols of sulfur × molecular weight of salt = grams of salt/l

| | | |
|---|---|---|
| Sulfate sulfur | 1.06 × 116 = | 122.96 g $(NH_4)_2SO_3$/l |
| Bisulfite sulfur | 3.41 × 99 = | 337.59 g $NH_4HSO_3$/l |
| Sulfate sulfur | 0.63 × 132 = | 83.16 g $(NH_4)_2SO_4$/l |
| Total salt | | 543.71 g/l |

### Total $SO_2$, Mols of $SO_2$/Liter as Sulfite and Bisulfite

#### $SO_2$ as Sulfite

Mols $SO_2$/l as sulfite = mols sulfite sulfur/l × 1.0

= 1.06 × 1.0

= 1.06 mols

#### $SO_2$ as Bisulfite

Mols $SO_2$/l as bisulfite = mols bisulfite sulfur/l x 1.0
= 3.41 x 1.0
= 3.41 mols

#### Total $SO_2$

Total $SO_2$ = $SO_2$ as sulfite + $SO_2$ as bisulfite
= 1.06 + 3.41
= 4.47 mols/l

### Active $NH_3$, Mols of $NH_3$/Liter as Sulfite and Bisulfite

#### $NH_3$ as Sulfite

Mols $NH_3$/l as sulfite = mols sulfite sulfur/l x 2.0
= 1.06 x 2.0
= 2.12 mols/l

#### $NH_3$ as Bisulfite

Mols $NH_3$/l as bisulfite = mols bisulfite sulfur/l x 1.0
= 3.41 x 1.0
= 3.41 mols/l

#### Active $NH_3$

Active $NH_3$ = $NH_3$ as sulfite + $NH_3$ as bisulfite
= 2.12 + 3.41
= 5.53 mols/l

### Total $NH_3$, Mols of $NH_3$/Liter as Sulfite, Bisulfite, and Sulfate

#### $NH_3$ as Sulfate

Mols $NH_3$/l as sulfate = mols sulfate/l x 2.0
= 0.63 x 2.0
= 1.26 mols/l

### Total $NH_3$

Total $NH_3$ = $NH_3$ as sulfite + $NH_3$ as bisulfite + $NH_3$ as sulfate

= 2.12 + 3.41 + 1.26

= 6.79 mols/l

### Reaction water ,Grams $H_2O$/Liter Combined with $SO_2$ and $NH_3$

$$2NH_3 + SO_2 + H_2O \rightarrow (NH_4)_2SO_3$$

$$NH_3 + SO_2 + H_2O \rightarrow NH_4HSO_3$$

$$2NH_3 + SO_2 + H_2O + 1/2\ O_2 \rightarrow (NH_4)_2SO_4$$

### Reaction Water in Sulfite (grams $H_2O$/l)

Reaction water ($SO_3^=$) = mols $SO_2$ as sulfite x 1.0 x 18g$H_2O$/g mol

= 1.06 x 1.0 x 18

= 19.08 g/l

### Reaction Water in Bisulfite (mols $H_2O$/l)

Reaction water ($HSO_3^-$) = mols $SO_2$ as bisulfite x 1.0 x 18 g$H_2O$/g mol

= 3.41 x 1.0 x 18

= 61.38 g/l

### Reaction Water in Sulfate (mols $H_2O$/l)

Reaction water ($SO_4^=$) = mols $SO_2$ as sulfate x 1.0 x 18 g$H_2O$/g mol

= 0.63 x 1.0 x 18

= 11.34 g/l

Free water, Grams $H_2O$/Liter - Unreacted

Free water = (specific gravity x 1000) - total salt g/l

= (1.226 x 1000) - 543.71

= 1226 - 543.71

= 682.29 g/l

C Value (mols total $NH_3$/100 mols $H_2O$)

$$C = \frac{(\text{Mols total } NH_3)(1800)}{(\text{free water}) + [\text{reaction water } (SO_3^=) + \text{reaction water } (HSO_3^-) + \text{reaction water } (SO_4^=)]}$$

$$C = \frac{6.79\ (1800)}{(682.29) + (19.08 + 61.38 + 11.34)}$$

$$C = \frac{12,222}{682.29 + 91.80} = \frac{12,222}{774.09}$$

C = 15.78 mols total $NH_3$/100 mols $H_2O$

$C_A$ Value (mols active $NH_3$/100 mols $H_2O$)

$$C_A = \frac{(\text{mols active } NH_3)\ 1800}{(\text{free water}) + [\text{reaction water } (SO_3^=) + \text{reaction water } (HSO_3^-) + \text{reaction water } (SO_4^=)]}$$

$$C_A = \frac{5.53\ (1800)}{(682.29) + (19.08 + 61.38 + 11.34)}$$

$$C_A = \frac{9,954}{682.29 + 91.80} = \frac{9,954}{774.09}$$

$C_A$ = 12.85 mols active $NH_3$/100 mols $H_2O$

A Value [mols $(NH_4)_2SO_4$/100 mols $H_2O$]

$$A = \frac{(\text{mols sulfate sulfur/l})\ 1800}{(\text{free water}) + [\text{reaction water } (SO_3^=) + \text{reaction water } (HSO_3^-) + \text{reaction water } (SO_4^=)]}$$

$$A = \frac{(0.63)(1800)}{682.29 + 91.80} = \frac{1,134}{774.09}$$

A = 1.46 mols $(NH_4)_2SO_4$/100 mols $H_2O$

**S Value (mols $SO_2$/100 mols $H_2O$)**

$$S = \frac{(\text{Total } SO_2,\ \text{Mols/l})(1000)}{(\text{free water}) + (\text{reaction water } (SO_3^=) + \text{reaction water } (HSO_3^-) + \text{reaction water } (SO_2))}$$

$$S = \frac{(8.05)(1000)}{(682.29) + (19.08 + 61.38 + 11.34)}$$

$$S = \frac{8{,}046}{774.09}$$

$S$ = 10.39 mols $SO_2$/100 mols $H_2O$

**$S/C_A$ Ratio (mols $SO_2$/mols active $NH_3$)**

$S/C_A$ = mols total $SO_2$/mols active $NH_3$

$S/C_A = 4.47/5.53$

$S/C_A = 0.81$

VAPOR PRESSURES OF $SO_2$, $NH_3$, AND $H_2O$ CALCULATED BY MODIFIED JOHNSTONE EQUATIONS (6)

**$SO_2$ Vapor Pressure of Absorber Liquor (mm Hg) at 126°F**

$$SO_2 \text{ Vapor Pressure} = P_{SO_2} = \frac{MS\,(2\,S/C_A - 1)^2}{S/C_A\,(1 - S/C_A)}$$

$$\text{where } \log_{10} M = 5.865 - \frac{2369}{\text{liquor temperature, °K}}$$

$$= 5.865 - \frac{2369}{325.37}$$

$$\log_{10} M = -1.416$$
$$M = 0.0384$$

$$P_{SO_2} = \frac{(0.0384)(10.39)[(2 \times 0.81) - 1]^2}{0.81\ (1 - 0.81)}$$

$$P_{SO_2} = \frac{0.1534}{0.1539}$$

$P_{SO_2}$ = 0.996 mm Hg

## $NH_3$ Vapor Pressure of Absorber Liquor (mm Hg) at 126°F

$NH_3$ vapor pressure = $P_{NH_3} = \frac{NC(1-S/C_A)}{2\,S/C_A - 1}$

where $\log_{10}N = 13.680 - \frac{4987}{\text{liquor temperature, °K}}$

$\log_{10}N = 13.680 - \frac{4987}{325.37}$

$\log_{10}N = -1.647$

$N = 0.0225$

$P_{NH_3} = \frac{(0.0225)(15.78)(1-0.81)}{(2 \times 0.81) - 1}$

$P_{NH_3} = \frac{0.0675}{0.620}$

$P_{NH_3} = 0.108$ mm Hg

## $H_2O$ Vapor Pressure of Absorber Liquor (mm Hg) at 126°F

$H_2O$ vapor pressure = $P_{H_2O} = P_W \times \frac{(100)}{[100 + C_A + S + (3 \times A)]}$

where $P_W$ = vapor pressure of pure water at 126°F

$P_{H_2O} = 103.31 \times \frac{100}{[100 + 12.85 + 10.39 + (3 \times 1.46)]}$

$P_{H_2O} = \frac{10,331}{127.62}$

$P_{H_2O} = 80.95$ mm Hg

CALCULATING THE VAPOR PRESSURE OF $SO_2$ (ppm) NECESSARY TO CAUSE A FUME ABOVE OR BELOW A TRAY USING MOORE'S FUME EQUATION

$$\log_{10}P_{SO_2} = \frac{-2102}{T} + 4.3134 + 2\log_{10}\left[\frac{(100 + C_A + S + 3A)\,(2S-C_A)}{(C_A + 2A)\,(C_A - S)}\right]$$

where T is the tray liquor temperature in °K = 325.37

$$\log_{10} P_{SO_2} = \frac{-2102}{325.37} + 4.3134$$

$$+ 2 \log_{10} \frac{[100 + 12.85 + 10.39 + (2 \times 1.46)][(2 \times 10.39) - 12.85]}{[12.85 + (2 \times 1.46)]\,(12.85 - 10.39)}$$

$$\log_{10} P_{SO_2} = -2.1469 + 2 \log_{10} 26.087$$

$$\log_{10} P_{SO_2} = 2.1469 + 2.8328$$

$$\log_{10} P_{SO_2} = 0.6859$$

$$P_{SO_2} = 4.852 \text{ mm Hg}$$

$$P_{SO_2}\ (\text{ppm}) = \frac{4.852 \text{ mm Hg}}{760 \text{ mm Hg}} \times 10^6$$

$$P_{SO_2}\ (\text{ppm}) = \underline{6{,}384}$$

# APPENDIX C

# CORROSION DATA

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C-3 Corrosion Tests in the Ammonia Absorption - Ammonium Bisulfate Regeneration Pilot Plant . . . 95

# APPENDIX C

## CORROSION DATA

Corrosion tests were made in the pilot plant during the following periods of operation: December 3-14, 1973 (period A) and July 2-18, 1975 (period B). The test specimens were immersed in the prewash sump liquor and in the gas duct leading from the prewash section. The first prewash section (period A) was made of 316L SS and was operated in an open-loop mode. The unit was susceptible to the highly corrosive prewash liquor (pH = 2.7) even with a purge rate of 15 gallons per minute of fresh water through the prewash. The metal surfaces exposed to the gas phase were severely pitted (40 to 60 mils deep). Based on these factors a second prewash was designed and constructed of fiberglass-reinforced plastic (period B). The FRP prewash was operated in a closed-loop manner and was impervious to the prewash liquor (pH = 1.0).

Table C-1 lists the trade name, base type, and manufacturer of each of the nonmetallic materials tested. Tables C-2 and C-3 list the various corrosion data and material evaluations.

During period A, specimens of Type 316L, Type 201, Type 304-L, USS 18-18-2 stainless steels, Carpenter 20, mild steel, neoprene, and Bondstrand 4000 were tested. The test results are listed in Table C-2.

The corrosion rates for stainless steels in the venturi sump liquor (with the exception of 18-18-2) were less than 2 mils/yr. Either pitting or crevice corrosion or both occurred on each specimen. The corrosion rate for USS 18-18-2 was 54 mils/yr with minute pitting and attack in the heat-affected zone of the weld.

The corrosion rates for the stainless steels tested in the gas duct ranged from 42 to 146 mils/yr with crevice corrosion occurring on each specimen. The specimens in the gas duct were wetted by about 2.5 gallons per hour of mist from the venturi sump. The mist contained sulfur dioxide in equilibrium with the flue gas stream containing about 2400 ppm sulfur dioxide and had a pH of about 1 (compared with an average pH of 2.7 in the sump). The lower pH accounts for the higher corrosion rates experienced in the gas ducts. Mild steel corroded at excessively high rates in both locations (580-2200 mils/yr).

TABLE C-1. NONMETALLIC MATERIALS TESTED IN THE PILOT PLANT FOR REMOVAL OF SULFUR DIOXIDE BY THE AMMONIA ABSORPTION PROCESS

| Trade name | Base type | Manufacturer |
|---|---|---|
| Bondstrand 4000 | Epoxy, fiberglass reinforced | Ameron<br>201 N. Berry Street<br>Brea, CA 92612 |
| Kerolite, blue | Polyethylene | Kearny Fluid Equipment, Inc.<br>Raritan, NJ 08869 |
| Koroseal | Polyvinyl chloride | B.F. Goodrich Industrial Products Company<br>Tuscaloosa, AL 35403 |
| Polypropylene | Polypropylene, rigid | American Viscose Corporation<br>Philadelphia, PA 35403 |
| Neoprene (sheet) | Chloroprene polymer | |
| Rubber, butyl (covered mild steel) | Isobutylene-isoprene, Gates No. 26,666 | Gates Rubber Company<br>999 S. Broadway<br>Denver, CO 80217 |
| Rubber, natural gum (covered mild steel) | Polyisoprene, Gates No. 1375 | Gates Rubber Company<br>999 S. Broadway<br>Denver, CO 80217 |
| Rubber, neoprene (covered mild steel) | Chloroprene polymer, Gates No. 9150 | Gates Rubber Company<br>999 S. Broadway<br>Denver, CO 80217 |

TABLE C-2. CORROSION TESTS IN THE AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION PILOT PLANT

(December 3-14, 1973)

| | Location of specimen | |
|---|---|---|
| | Immersed in prewash sump | Sump outlet gas duct |
| Operating time, hr | 217 | 217 |
| Exposure conditions | | |
| Test medium | Sump liquor | Saturated flue gas |
| Solids, % by wt | 0.002[a] | - |
| pH | 2.8(2.0-3.9) | - |
| Flow rate | | |
| Gal/min | 30[b] | |
| Acfm | - | 3,060 |
| Temperature, °F | 117(101-124) | 122(115-133) |
| Chemical analysis, g/l | | |
| $SO_4$ (total sulfur) | 0.15(0.09-0.22) | - |
| Cl | 0.1(0.04-1.5) | Nil |
| Corrosion rate of metals, mils/yr[c] | | |
| Carpenter 20 Cb-3 welded to Carpenter 20 Cb-3 | <1, Pm | 50,[d] p-5 |
| Type 316L welded to type 316L | <1[d] | 42,[d] p-15 |
| Type 201 welded to type 316 | 1,[d] p-6 | 144,[d] p-8 |
| Type 304L welded to type 308L | 2,[d] Pm | 146,[d] 5-11 |
| USS 18-18-2 welded to Inconel 82 | 54,[e] Pm | 132,[d] Pm |
| Mild steel A-283 welded to E6012 | 7,200 | 580[d] |
| Condition of nonmetallic specimens[f] | | |
| Bondstrand 4000 | Good | Good |
| Neoprene (sheet 0.223 in. thick) | Good | Good |

a. On December 14, 1973 when dirty flue gas was used, the liquor contained 6.5% by wt of solids.
b. The average fresh water makeup during test period.
c. "p" preceding a number indicates pitting to a depth in mils shown by number; "Pm" indicates minute pits.
d. Crevice corrosion occurred under the Teflon spacer.
e. Localized attack occured in the heat-affected zone of the weld.
f. "Good" indicates no appreciable deterioration.

## TABLE C-3. CORROSION TESTS IN THE AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION PILOT PLANT

(July 2-18, 1975)

| | Location of specimen | |
|---|---|---|
| | Immersed in prewash sump | Downstream of prewash mist eliminator |
| Operating time, hr | 221[a] | 194[a] |
| Exposure conditions | | |
| Test medium | Sump liquor | Saturated flue gas |
| Solids, % by wt | 0.5 | - |
| pH | 1.0 | - |
| Chemical analysis[b] | | |
| Undissolved solids, % | 0.031 | - |
| Total dissolved solids, g/l | 72.0 | - |
| Sulfur as $SO_4$, g/l | 50.8 | - |
| Total iron, g/l | 7.8 | - |
| Cl, g/l | 6.0 | - |
| Ca, g/l | 0.9 | - |
| Al, g/l | 0.8 | - |
| K, g/l | 0.2 | - |
| Na, g/l | 0.1 | - |
| Temperature, °F | 127(125-130) | 136(126-150) |
| Corrosion rate of metals, mils/yr[c] | | |
| Carpenter 20 Cb-3 welded to Carpenter 20 Cb-3 | 3 | 38,[d] P-8 |
| Duriron, not welded | 1, P-11 | 6, P-25 |
| Hastelloy G welded to Hastelloy G | 1[e] | 5[e] |
| Illium P, not welded | 29[d] | 43,[d] P-9 |
| Inconel 625 welded to Inconel 625 | <1 | <1 |
| Inconel 600 welded to Inconel 82 | 1,156, P-1 | 118[d] |
| Inconel 825 welded to Inconel 135 | 6,[d] P-20 | 49,[d] P-11 |
| Type 316L welded to type 316L | 8,[d] P-15 | 65, P-9 |
| USS 18-18-2 welded to Inconel 82 | ≥890[f] | 66 |
| Evaluation of nonmetallic materials[g] | | |
| Kerolite, polyethylene | Poor | - |
| Koroseal, polyvinyl chloride | Good | Good |
| Polypropylene | Fair | Good |
| Rubber, butyl | Good | Good |
| Rubber, natural gum | Fair | Good |
| Rubber, neoprene | Good | Good |

---

[a] Because water (used 29 hr) or air (used 18 hr) is not corrosive to the alloys tested, the rates for the alloys in the sump were determined on the basis of 192 hr exposure and those in the duct 176 hr.

[b] Analysis of liquor from clarifier near end of test.

[c] "P" preceding a number indicates pitting during the exposure period to the depth in mils shown by the number.

[d] Crevice corrosion at Teflon insulator.

[e] Attack of weld.

[f] Specimen corroded to failure during test.

[g] Evaluation: good, little or no change in condition of specimen; fair, definite change--probably could be used; poor, failed or severely damaged.

Both nonmetallic materials showed good resistance to corrosion in both locations. The hardness of neoprene did not change appreciably during the test period. These short duration tests indicate that neoprene-lined equipment resists attack downstream from the venturi element where temperature is not a factor (the maximum temperature in the gas duct was 133°F; the maximum recommended operating temperature for neoprene is 150°F). Long duration tests are needed to evaluate neoprene fully.

Corrosion test specimens of nine alloys, three plastics, and three rubbers were exposed during particulate removal efficiency tests carried out in period B. The test results are listed in Table C-3.

The specimens in the sump were immersed a total of 221 hr (192 hr in scrubber liquor and 29 hr in water). Specimens in the gas duct downstream from the mist eliminator were exposed for 176 hr of operation with flue gas and for 14 hr with air for a total of 190 hr. The pilot-plant equipment and the test specimens were washed clean at the beginning of each idle period.

Corrosion of alloys by water or air at temperatures of 125° to 150°F is usually negligible. Therefore, the rates of attack of alloy specimens in the sump were determined on the basis of 192 hr of exposure to scrubbing liquor and those in the duct on a basis of 176 hr of exposure to treated flue gas. However, the total exposure periods were considered in evaluation of the nonmetallic materials.

The corrosion rates for the alloys ranged from less then 1 mil/yr for Inconel 625 in both tests to 1126 mils for Incoloy 800 in the sump liquor. Six of the nine alloys had lower rates in the liquor than in the flue gas. Two alloys, Incoloy 800 and USS 18-18-2 were corroded at higher rates by the liquor; their rates were excessively high (<890 and 1126 mils/yr). Duriron and Hastelloy G each had rates of 1 mil/yr in the liquor and 5 mils in the gas. Carpenter 20 Cb-3 had a low rate, 3 mils/yr, in the liquor, but the rate was 38 mils with pitting in the gas. Inconel 625 was the only alloy not affected by localized attack in both test locations.

The three rubbers and two plastics tested in the treated flue gas duct showed good resistance to deterioration. The conditions were more severe for the specimens immersed in the liquor sump. Three materials were in good condition-Koroseal (PVC), butyl, and neoprene. Polypropylene and natural rubber were in fair condition. Kerolite, a polyethylene coating, failed. No change was detected in the Durometer A hardness of the three rubbers and of Koroseal exposed in the sump or in the gas duct.

# APPENDIX D

# EQUIPMENT EVALUATION

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## APPENDIX D

## EQUIPMENT EVALUATION

### EQUIPMENT FOR THE PILOT PLANT

### Ductwork to Pilot Plant

No maintenance was required on the 16-in.-diameter rigid mild steel ductwork used for transporting the flue gas to the pilot plant. A 1/2- to 1-in. scale and flyash buildup protected the duct from the condensing $SO_3$ acid mist in the inlet flue gas.

### Gas Prewash Section No. 1

The initial venturi section was a 1-ft-square duct constructed of 1/4-in. type 316L stainless steel. Rods (3/4-in. type 316 SS pipe) were laid across the venturi throat perpendicular to the gas flow. The number of rods was changed to vary the pressure drop across the venturi throat. The venturi section was mounted on a sump constructed of 10-gage type 316L SS. The venturi sump was the reservoir for the recirculating prewash liquor and also channeled the conditioned gas into the type 316L SS ductwork (14-in. O.D.) leading to the absorber.

The venturi housing was severely damaged by erosion and corrosion and was replaced, after 650 hr of operation, with one coated with urethane. Urethane was used to protect the steel from the low pH (1.5 to 3.0) liquor and the abrasive flyash in the recirculating liquor. The urethane coating in the upper portion of the venturi throat was completely destroyed after 700 hr of operation. The rods (316 SS) across the venturi throat were badly pitted and needed replacing. The sump was inspected after 2,000 hr of operation. The walls of the sump were corroded and showed heavy pitting above the normal gas-liquid interface. The SS ductwork from the sump to the absorber also was severely pitted.

The initial gas prewash unit was not equipped with a mist eliminator between the venturi section and the absorber. Mist, which contained flyash solids and dissolved materials, was carried by the gas stream to the absorber. The absorber product liquor was diluted and its contaminant level increased.

### Gas Prewash Section No. 2

A second gas pretreatment section was designed and constructed of fiberglass reinforced plastic (FRP) (Atlac 382) and coated internally with an epoxy resin paint. The venturi throat was lined with a 1/8 in.-thick neoprene skirt while the rod supports were made from 1/2-in. neoprene. The unit was equipped with a plastic chevron mist eliminator (Heil Process Equipment Company) mounted internally in the horizontal run. A schematic drawing of this prewash unit was shown in Figure 7 (see text). Figure D-1 is a photograph of the prewash unit installed in the pilot plant.

The FRP and neoprene rubber were impervious to the low pH (1.0) corrosive sump liquor and the abrasive flyash in the liquor. Stainless steel fittings and spray nozzles failed and had to be replaced periodically. The original rods in the venturi throat, made from 3/4-in. type 316 SS pipe, were replaced with CPVC pipe.

With a pressure drop of 10 in. of water across the venturi throat and a liquor/gas (L/G) ratio of 20 (approximately 35 gpm of recirculating wash liquor), the prewash humidified and cooled the flue gas before the gas entered the absorber. The chevron mist eliminator decreased the mist carryover into the absorber to 1 $ml/m^3$ (2.09 x $10^{-5}$ gal/1000 $ft^3$).

## Settling Tank

A settling tank constructed of FRP (Atlac 382) was installed in the prewash liquor loop to remove the undissolved solids from the recirculating sump liquor. The sump liquor was purged to the settling tank at 0.5 or 1 gpm. These rates correspond to clarified liquor residence times of 8 and 4 hr, respectively. The settling tank is shown in Figure D-2. The unit performed well during short test runs. Long-term operations are needed to properly evaluate the unit.

## Absorbers

The basic absorber was comprised of 4-ft sections each 32 in. square. The sections were constructed of either type 304 or 316 SS. Three different configurations were tested as shown in Figures D-3, -4, and -5. The absorber of configuration D-3 originally had three beds of 3/4-in. glass marbles approximately 6 in. in depth. It was built by NDC, Environeering, Inc. The marbles on the lower stage were subject to thermal shock and cracking whenever cooler liquor came into contact with the heated bed. Liquor fall-through was a problem with the marble beds; in some instances the level was completely lost on a bed. Solids in the scrubbing liquor would agglomerate the marbles causing channeling of the liquor and gas streams resulting in liquor fall through and poor $SO_2$ removal efficiency. Therefore, this marble bed was replaced with a valve tray element (Koch Flexitray). A typical valve tray element is shown in Figure D-6. The efficiency of the valve tray element was similar to that of the

FLUE GAS INLET
ABSORBER INLET
PREWASH SECTION
SUMP

Figure D-1. Second prewash section (fiberglass reinforced plastic).

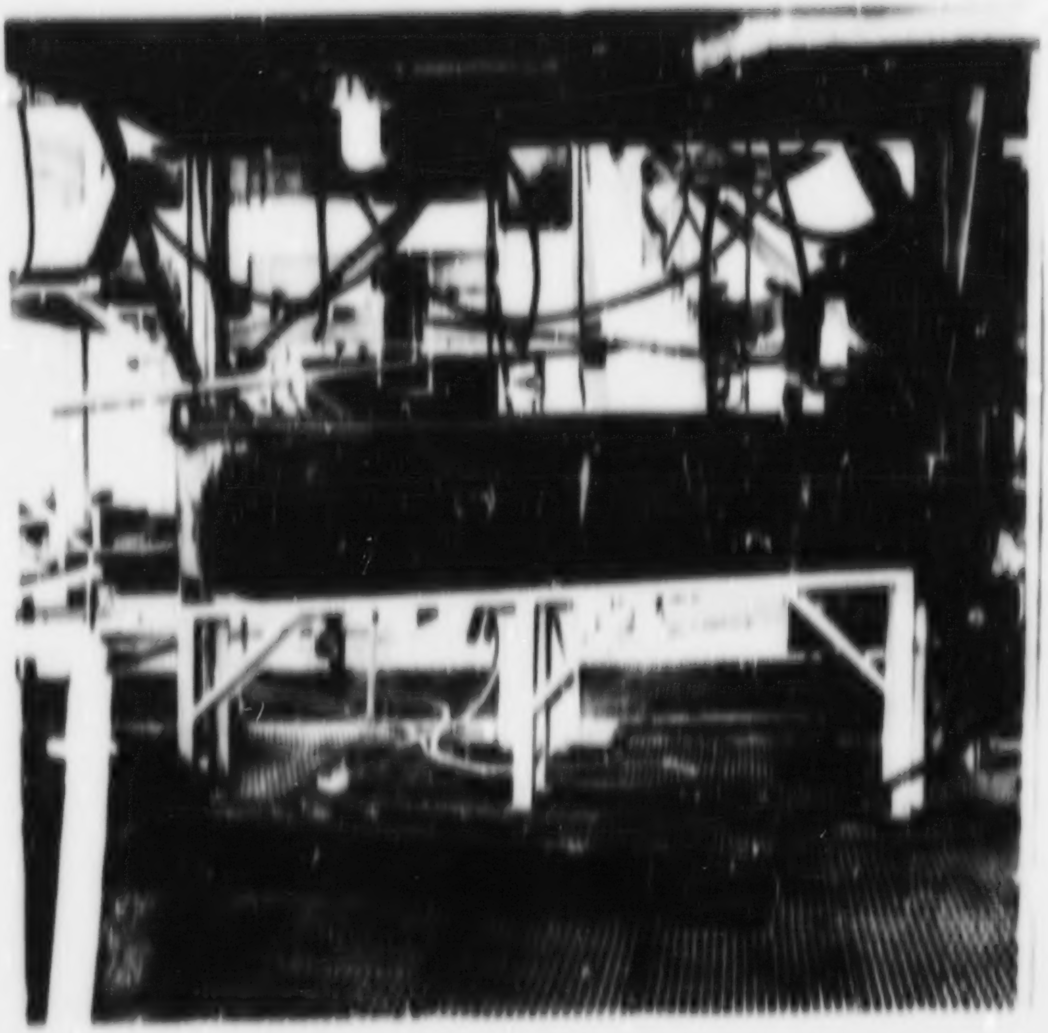

Figure D-2. Flyash settling tank in prewash section.

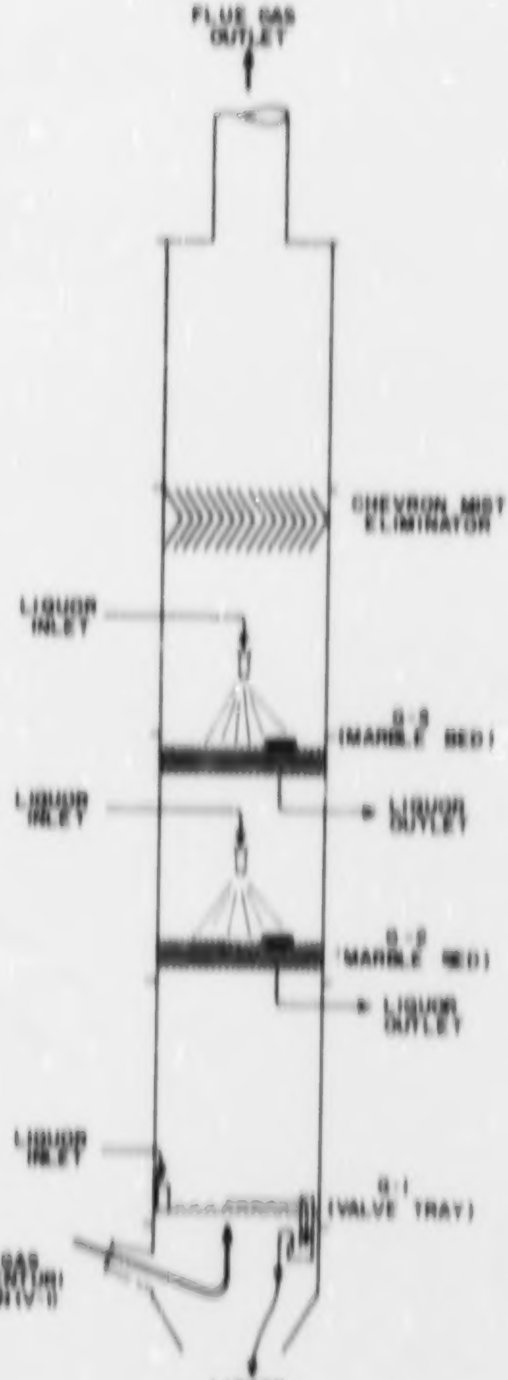
FLUE GAS
OUTLET
CHEVRON MIST
ELIMINATOR
LIQUOR
INLET
D-3
(MARBLE BED)
LIQUOR
INLET
LIQUOR
OUTLET
D-2
(MARBLE BED)
LIQUOR
OUTLET
LIQUOR
INLET
D-1
(VALVE TRAY)
FLUE GAS
LIQUOR
OUTLET

Figure D-3. Absorber configuration A.

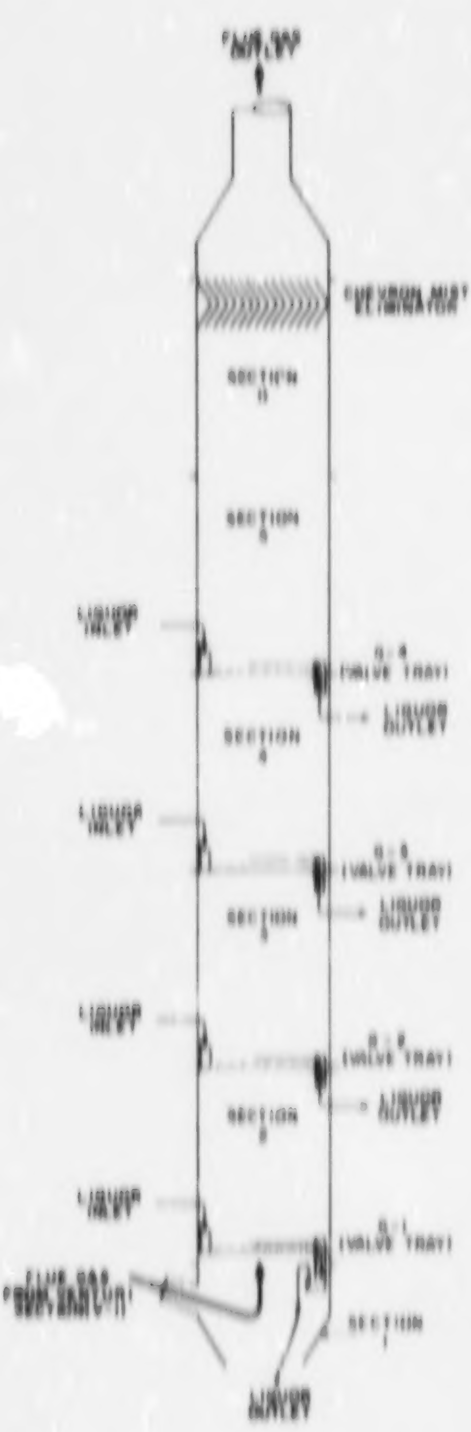
FLUE GAS OUTLET
CHEVRON MIST ELIMINATOR
SECTION 6
SECTION 5
LIQUID INLET
D-4 (VALVE TRAY)
LIQUID OUTLET
SECTION 4
LIQUID INLET
D-3 (VALVE TRAY)
LIQUID OUTLET
SECTION 3
LIQUID INLET
D-2 (VALVE TRAY)
LIQUID OUTLET
SECTION 2
LIQUID INLET
D-1 (VALVE TRAY)
FLUE GAS
SECTION 1
LIQUID OUTLET

Figure D-4. Absorber configuration B.

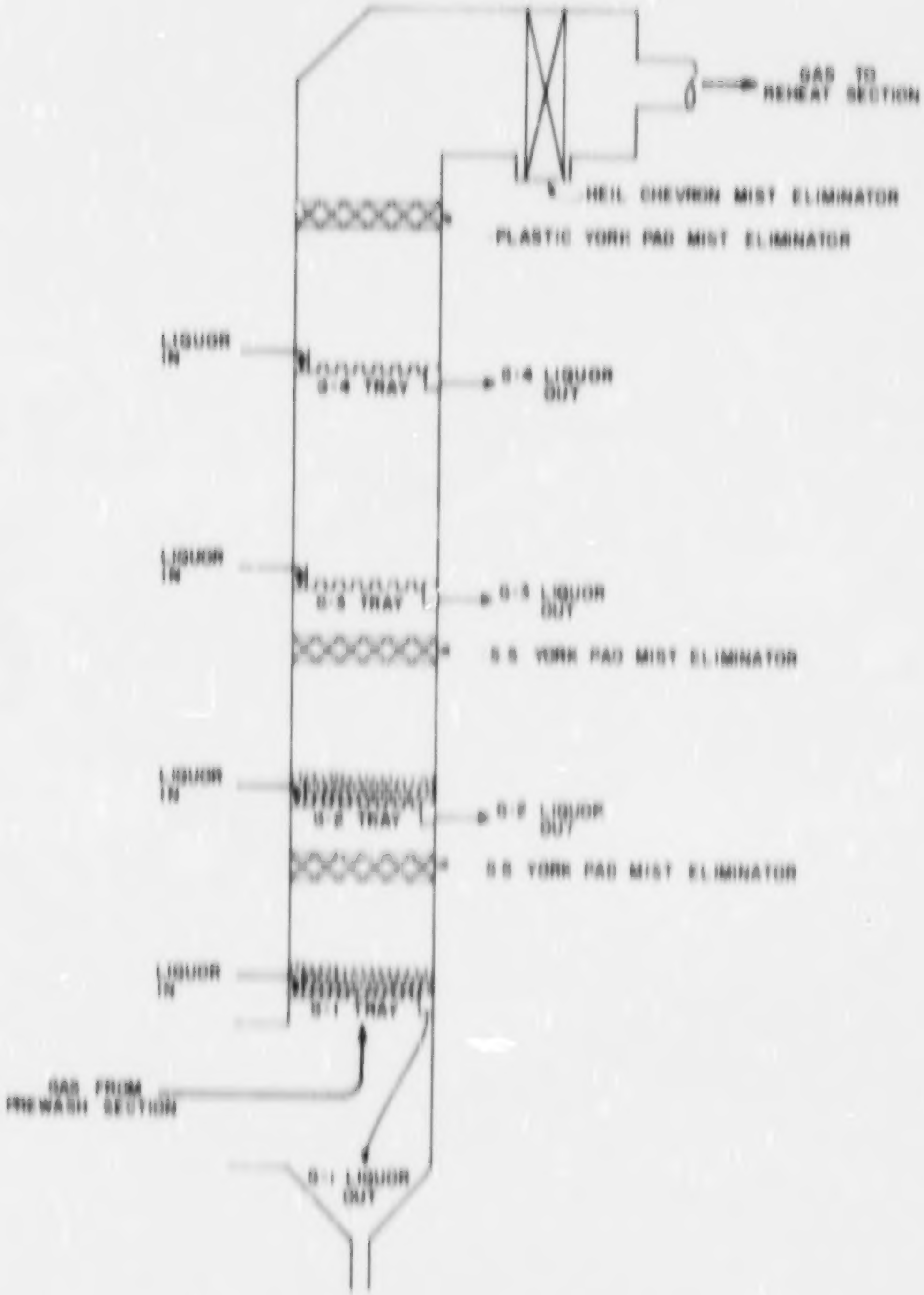
GAS TO
REHEAT SECTION
HEIL CHEVRON MIST ELIMINATOR
PLASTIC YORK PAD MIST ELIMINATOR
LIQUOR
IN
D-4 TRAY
D-4 LIQUOR
OUT
LIQUOR
IN
D-3 TRAY
D-3 LIQUOR
OUT
S.S. YORK PAD MIST ELIMINATOR
LIQUOR
IN
D-2 TRAY
D-2 LIQUOR
OUT
S.S. YORK PAD MIST ELIMINATOR
LIQUOR
IN
D-1 TRAY
GAS FROM
PREWASH SECTION
D-1 LIQUOR
OUT

Figure D-5. Absorber configuration C.

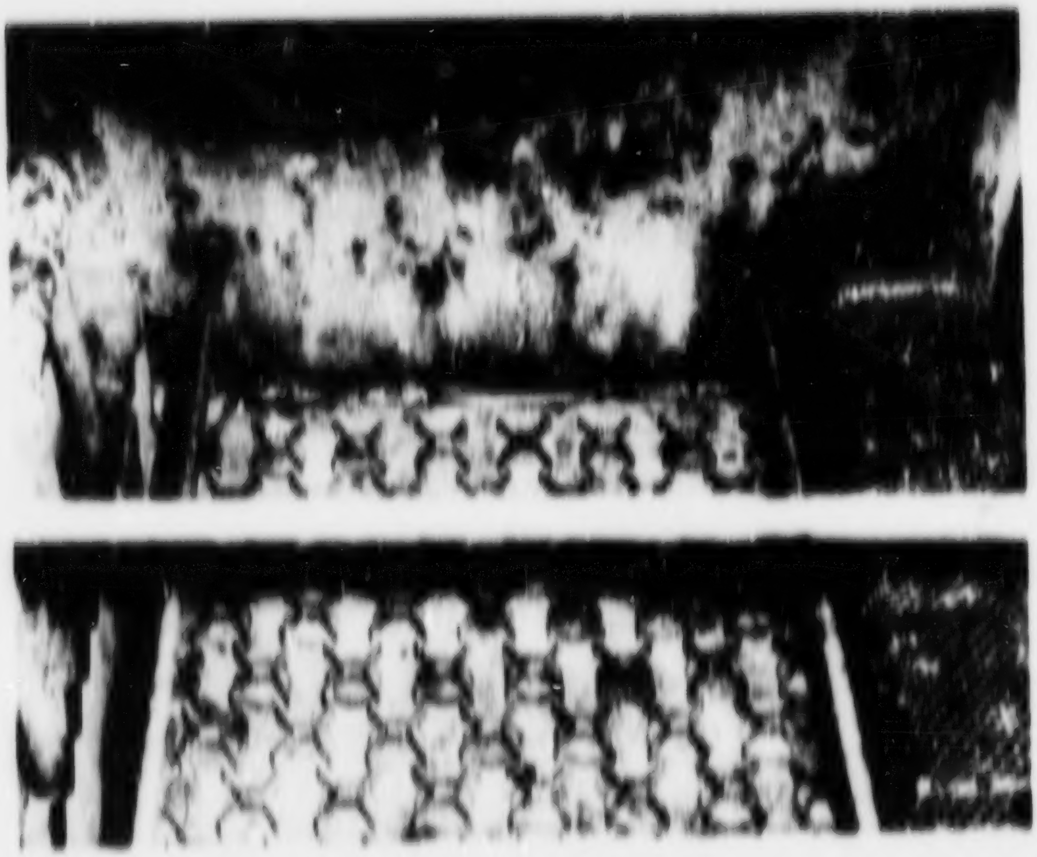

Figure D-6. Koch flexitray.

marble bed; approximately 35% of the $SO_2$ to the absorber was removed on the first stage.

The two remaining marble beds later were replaced with valve tray elements, and a fourth valve tray was added as a water wash to decrease the quantity of ammoniacal salts in the entrained mist leaving the absorber (see Figure D-4, configuration B). Entrained mist would be evaporated in a shell-and-tube reheat element leaving scale deposits on the reheater tubes.

Each valve tray element has an adjustable dam in the liquor outlet weir box. The liquor level on each tray could be varied from 0 to 3 in. A series of air and water tests determined that a liquor depth of 2 in. on each tray and a gas flow rate of 2,800 acfm (125°F) were necessary to minimize liquor transfer from stage to stage.

The four-stage absorber was adequate to produce ammoniacal liquors for regeneration test programs. However, several problems existed in the absorber performance area. The valve tray elements were prone to transfer liquor from one stage to another, therefore, true stage separation was not achieved. The $SO_2$ removal efficiency of the bottom two stages was very poor; the Murphree tray efficiencies for stages G-1 and G-2 averaged 43.6% and 66.1%, respectively. A three-pass chevron mist eliminator, mounted above the fourth stage in the vertical run, was ineffective in preventing mist carryover from the absorber.

Further modifications to the absorber resulted in the final tower arrangement (configuration C) shown in Figure D-5. Mobile plastic spheres (1-in.-diameter) were poured onto stages G-1 and G-2 to a depth of 12 in. These spheres increased the average Murphree efficiencies to 90% and 92% for stages G-1 and G-2, respectively. Also, installation of SS wire mesh pads prevented excessive mist carryover from stage to stage. A chevron mist eliminator (Heil Process Equipment Corporation), mounted in a horizontal run after the fourth stage, gave improvement but the mist carryover still exceeded the standard limit of 110 mg/m³. After a plastic York mesh pad mist eliminator was installed between the fourth stage and the Heil mist eliminator, mist carryover decreased to 70.6 mg/m³, well below the standard.

The final absorber configuration improved control of absorber liquor concentrations and $SO_2$ removal and decreased mist carryover to acceptable levels. However, liquor fall through (weepage) continued to be a problem in the vertical configuration and resulted in less than true stage separation. It is possible that a horizontal-packed absorber would solve this problem.

## Exit Gas Reheat System

The exit flue gas was reheated to 175°F in most tests with an in-line, indirect steam-heated reheater. The heat exchanger element contained 234 (12 rows) 1-in.-O.D. by 20-in.-long tubes. The heat transfer area was 102.4 $ft^2$. The tubes were constructed of the following materials: Inconnel 625, Incoloy 825, 316L SS, Cor-Ten A, and Hastelloy C-276. A reheat module is shown in Figure D-7.

The calculated overall heat transfer coefficient (Uo) ranged from 14.8 to 27.6 Btu/(hr)($ft^2$)(°F). The pressure drop across the tube banks averaged 0.9 in. of water. The unit required no maintenance except for removing scale deposits. Before the plastic mesh-pad mist eliminator was installed ahead of the exit chevron mist eliminator, heavy mist carryover resulted in the buildup of scale on the tubes as shown in Figure D-8. The scale consisted largely of ammonium sulfate and ammonium chloride. The reheat element dissipated the water vapor in the scrubbed flue gas but did little to reduce the opacity of the ammonia-sulfur plume.

## Blower System

The flue gas was moved through the system with three fans; two constant-speed drive fans ahead of the absorber and a variable-speed drive fan after the absorber. The two constant-speed fans were installed in series. All of the fans were manufactured by American Standard and were constructed of 1/4-in. type 304L SS plate. The fans were V-belt driven by 40-hp motors and were rated for 4,000 acfm at 300°F. They were operated so that the bottom of the absorber was under a slight pressure and the top under a slight vacuum.

The blowers were relatively maintenance free. Flyash deposits in the blower housings were minimal since the flue gas was drawn from downstream of the electrostatic precipitators. One set of fan bearings was replaced after approximately 3,500 hr of operation. The fluid drive on the variable-speed fan required priming after lengthy periods of inactivity.

## Pumps

Scrubbing liquor was circulated to three of the four absorber stages (S-1, S-2, and S-3) with Allen-Sherman-Hoff (A-S-H) centrifugal pumps. The A-S-H pumps were of split housing construction with removable neoprene rubber linings and neoprene-coated impellers. The pumps were coupled to their respective motors (15-hp General Electric) by American Standard (Gyrol) fluid drives. The fourth absorber stage (S-4) was fed with a Wilfley centrifugal pump. The casing and impeller were constructed of type 316L SS. The Wilfley pump was V-belt driven with a 15-hp General Electric motor.

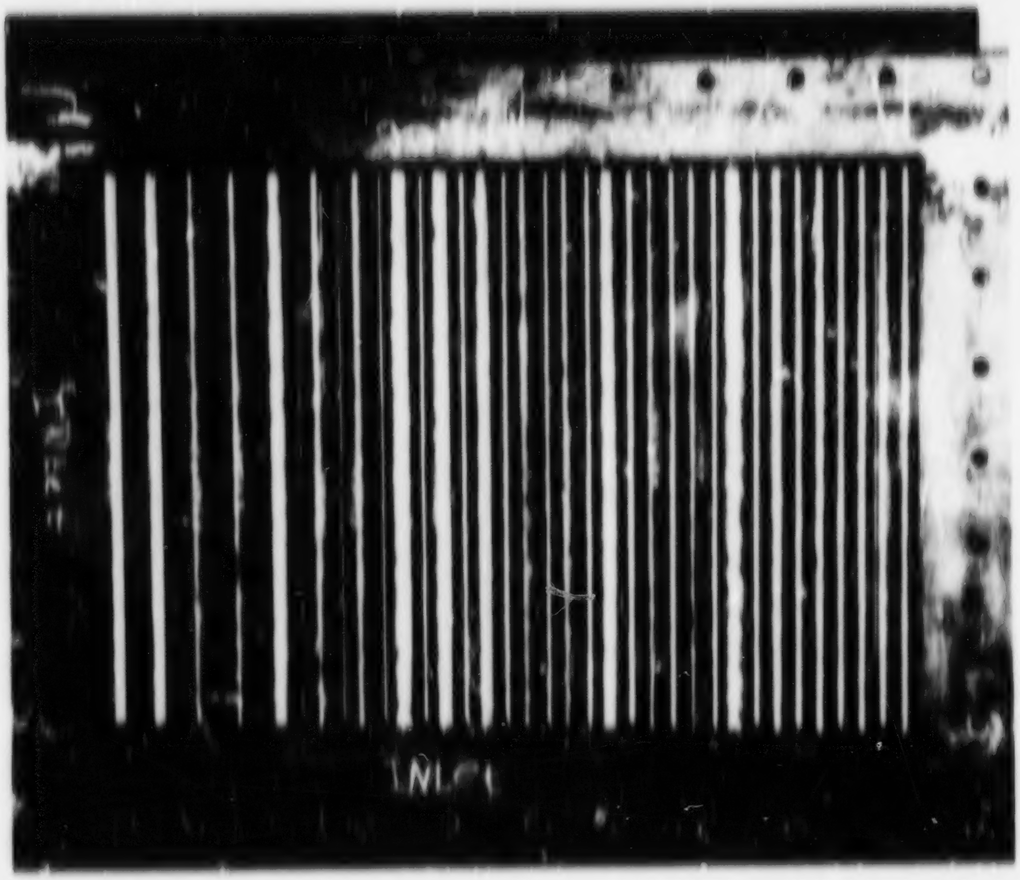

Figure D-7. Module for reheating stack gas with indirect steam.

Figure D-8. Fouled reheat module.

All of the A-S-H and the Wilfley pumps gave excellent service with minor problems. No noticeable wear was observed in the rubber linings or on the rubber-coated impellers. The main problem area with the A-S-H pumps was in the automatic control loop. The control motor would not regulate the speed of the pump motor. Changes in the pumping rates were made manually. Some shaft leakage occurred with the Wilfley pump while circulating liquors with high specific gravities (1.25). Some of the mechanical seals stuck because of solids. Other Wilfley pumps gave excellent service in general use.

The A-S-H pump unit supplied with the evaporator-crystallizer failed in two areas. The pump motor was undersized (3 hp) and burned out within 200 hr of operation. The motor was replaced with a 15-hp motor which functioned satisfactorily. The neoprene lining on the suction and shell side of the pump was damaged by erosion and chemical attack. (Original specifications called for Hypalon linings but neoprene was supplied inadvertently.) The erosion resulted from contact with the $(NH_4)_2SO_4$ crystals and the chemical attack from the high temperature sulfate solution. The literature indicates that neoprene is resistant to $(NH_4)_2SO_4$ slurries at temperatures to 212°F though the maximum recommended temperature is 150°F. The temperature in the crystallizer reached 205°F for short periods of time. The suction side of the impeller was completely destroyed and the underlying mild steel severely corroded. The neoprene liners were replaced with Hypalon liners and the impeller was replaced with a Hypalon-coated impeller. The operating temperature of the crystallizer was restricted to 175°F and the pump performed satisfactorily during the remaining test programs.

An A-S-H pump (split housing, 3-in. suction, neoprene lined, and V-belt driven) was used to recirculate the prewash liquor in the venturi sump. There was no corrosion from the low pH (1.0) liquor nor any erosion from the undissolved solids (flyash).

A Tuthill gear pump, used to pump absorber product liquor to the storage tanks, performed satisfactorily in all tests.

A Jabsco pump (1-in. suction, air driven) failed to consistently pump the $(NH_4)_2SO_4$ slurry (15% solids) from the evaporator-crystallizer to a filter. The pump was unable to maintain suction against the high vacuum (20 in. mercury) in the crystallizer. The plastic impeller blades broke off during the infrequent periods when the pump was able to move the slurry. With a motor-driven Jabsco pump inserted into a recirculation feed loop at near atmospheric suction pressure, it was able to pump a 10% $(NH_4)_2SO_4$ crystal slurry continuously to and from a centrifuge in the sulfate separation section.

## Acidulator-Stripper No. 1

The first acidulator-stripper unit tested was used in both Phase II and Phase III. It was shown in Figure 10 (see text). The acidulator, 6 ft by 1 ft diameter, was constructed of type 316L SS schedule 10 pipe (wall thickness = 0.180 in.) and coated internally with Teflon. A mixing cone (316L SS) located near the top of the acidulator received the sulfuric acid and absorber product liquor streams. The mixed stream dropped from the cone to a pool of retained acidulant in the lower portion of the vessel. The stripper was the same size as the acidulator and was made of the same materials. It was packed with 54 in. of dumped 2-in. Tellerette packing rings. The rings rested on a Teflon-coated type 316 SS screen located approximately 6 in. from the bottom of the stripper. Both the acidulator and the stripper were oversize. Intimate mixing of the acid ion source (sulfuric acid) and the absorber product liquor to obtain complete acidulation was not achieved in the acidulator. Also, in the stripper, the packing irrigation rate (2.04 gal of acidulated liquor/min/ft² of packing cross sectional area) was insufficient to decrease the amount of free $SO_2$ in the effluent to 0.5 g/l.

The extremely corrosive acidulated material and the elevated liquor temperature caused material failure. The reaction of the sulfuric acid and the absorber product liquor is highly exothermic with temperatures at the point of mixing reaching as high as 190°F. The SS mixing cone was destroyed. The Teflon liner in the acidulator deteriorated and eventually separated from the vessel wall.

## Acidulator-Stripper No. 2

A corrosion resistant acidulator-stripper was constructed from 4-in. I.D., schedule 40 plexiglass and PVC tubing. This unit was used during most of the Phase III work. By trial and error, the acidulator evolved as a mixing pot connected to the stripper by a gravity overflow tube. A schematic drawing was shown in Figure 11 (see text). Figure D-9 is a photograph of the unit. The effective volume of the acidulator was 1.5 gal and the liquor residence time approximately 3 min at a combined liquid flow rate of 0.5 gpm. The $SO_2$ flashed in the acidulator was combined in a common vent system with the $SO_2$ released in the stripper.

The stripper design resulted from meetings with representatives of Cominco. The stripper contains 30 ft of dumped Tellerette packing. Stripping gas inlets were provided so that 10, 20, or 30 ft of packing could be used. With the reduced cross sectional area (0.087 ft²), a packing irrigation rate of 5.7 gal of acidulated material per square foot of packing cross sectional area and 5 ft³ of stripping gas per minute, the amount of free $SO_2$ remaining in the stripper effluent was decreased to

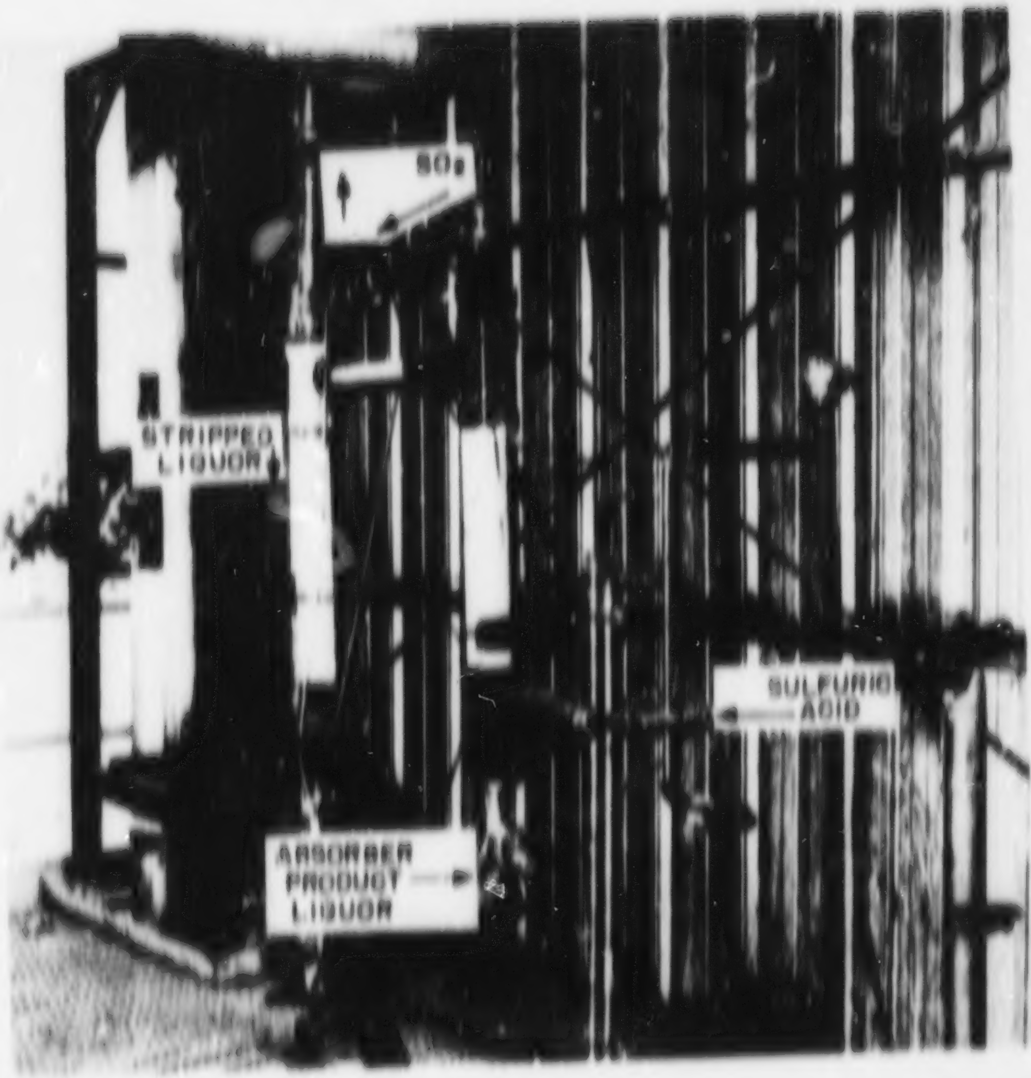
SO2
STRIPPED LIQUOR
SULFURIC ACID
ABSORBER PRODUCT LIQUOR

Figure D-9. Final acidulator-stripper.

0.5 g/l or less. The overall performance of acidulator-stripper was excellent with no maintenance problems.

### Evaporator-Crystallizer

The evaporator-crystallizer was designed and constructed by Goslin Division of Envirotech Corporation, Birmingham, Alabama. This Oslo-type single-effect crystallizer is shown in the schematic drawing in Figure D-10. The vaporizer chamber was 1 ft I.D. by 8.5 ft tall and rests on the crystallizer chamber which was 2 ft I.D. by 13-ft tall. A downcomer, extending from the vapor chamber down into the crystallizer, was 5 in. I.D. by 12 ft 8 in. tall. The mother liquor was heated externally in a tube-and-shell heat exchanger with low-pressure steam (50 psig). A direct contact (barometric) condenser and a steam ejector connected in series maintained the vacuum in the vapor chamber and also removed any chemical contaminants in the vaporizer off-gas. The steam ejector was powered with high-pressure steam (250 psig). The condenser and ejector are shown in Figure D-11. The entire unit and its piping were constructed from type 316L SS. The operating specifications required that the unit evaporate 200 lb/hr of water from the $(NH_4)_2SO_4$ solution at 170°F and 22 in. of mercury vacuum.

The overall performance of the unit was acceptable. The primary problem area was in establishing the operating parameters for the unit. The recommended steam pressure to the ejector (250 psig) was insufficient to maintain the desired 22 in. of mercury vacuum in the vaporizer section. As a result the mother liquor temperature exceeded 200°F and caused chemical attack on the heat affected zones (welds) in the unit. Increasing the steam pressure to 270 psig resulted in the desired vacuum and operating temperature (170°F). Solids buildup and eventual plugging of the downcomer and heat exchanger tubes resulted from operating the unit with a crystal loading of 20-30% by wt. At lower loading rates (10-15%) plugging did not occur and crystals of adequate size (70% plus 35 mesh) were produced.

The $(NH_4)_2SO_4$ crystals produced would not flow out of the evaporator by gravity and had to be pumped to the crystal separation equipment. An insulated 1-in. pipeline to the separation equipment plugged frequently during intermittent operation. A continuous recirculation feed loop was installed and eliminated plugging problems.

### Crystalline Ammonium Sulfate Separation Equipment

Two types of solids separation equipment were tested, a vacuum belt filter and a screen bowl centrifuge. The belt filter was an Eimco model 112 extractor horizontal belt filter as shown in Figure D-12. The continuous belt filter (10 ft² of vacuum

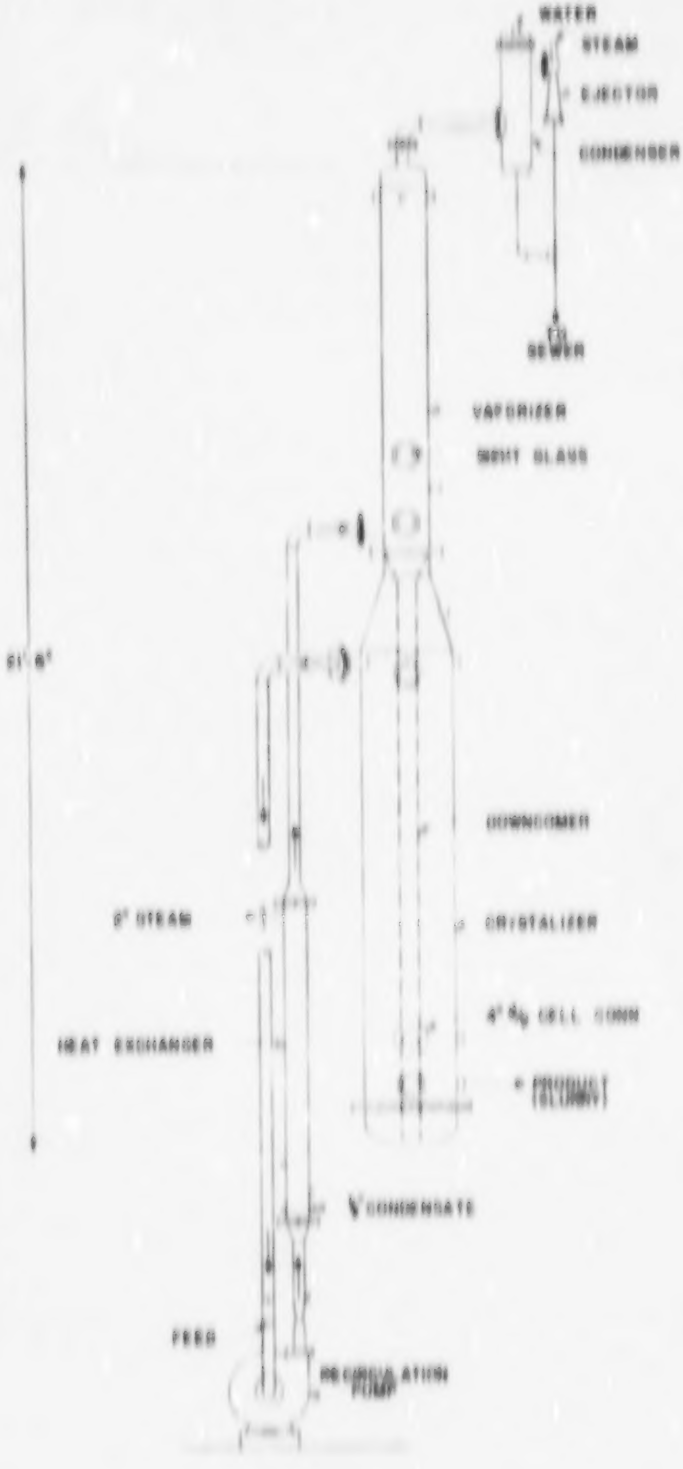
WATER
STEAM
EJECTOR
CONDENSER
SEWER
VAPORIZER
SIGHT GLASS
51' 6"
DOWNCOMER
3" STEAM
CRYSTALIZER
4" Δp CELL CONN
HEAT EXCHANGER
PRODUCT (SLURRY)
CONDENSATE
FEED
RECIRCULATION PUMP

Figure D-10. Oslo-type evaporator-crystallizer.

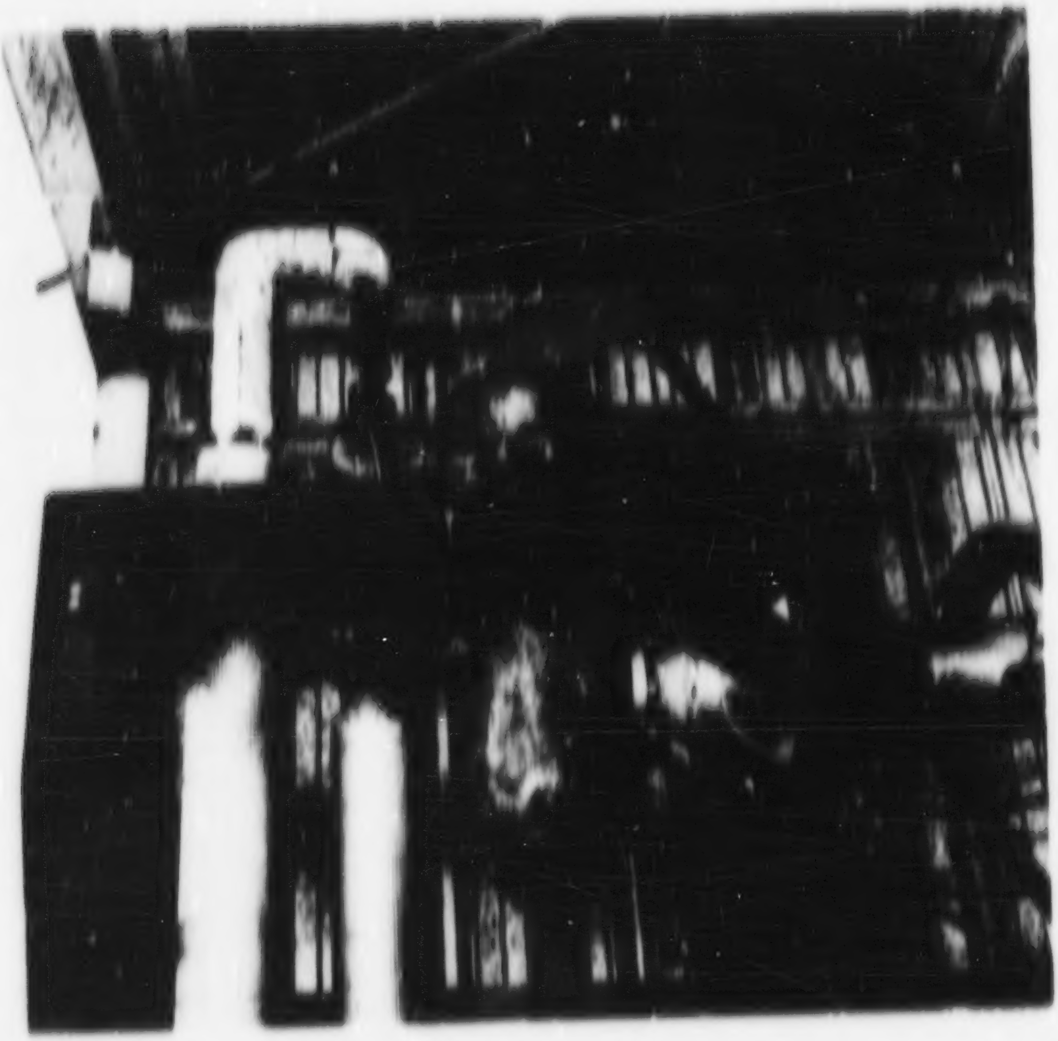

Figure D-11. Ejector-condenser.

Figure D-12. Eimco extractor horizontal belt filter.

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filter area) was skid mounted. The unit was self-contained with a variable-speed belt drive, a Nash vacuum pump, two supernatant liquor receiving tanks, and a pump to move the supernatant back to the crystallizer. The belt filter was too large for continuous operation. Sufficient material could not be maintained on the belt to prevent vacuum breaks even at the lowest belt speed (3 ft/min). In batch-wise operation, the unit removed $(NH_4)_2SO_4$ crystals at a rate sufficient to balance the production rate of 200 lb/hr. The crystals produced were sized about 70% plus 15 mesh and contained 5-10% moisture. The crystals were dried in a gas-fired rotary dryer to 2% moisture or less. The filter was maintenance free.

The centrifuge was a 6-in. continuous screen bowl centrifuge manufactured by Bird Machinery Company. The unit was constructed from type 316 SS. The screen bowl contained 0.008-in. circumfrential slots. Slurry from the evaporator-crystallizer was pumped continuously to the centrifuge through a recirculation feed loop. Sheaves were provided to permit operating the centrifuge at 3,000, 3,500, and 4,000 rpm corresponding to g-forces of 760, 1,040, and 1,350 lb force/lb mass.

The centrifuge gave acceptable service with few operational problems. A crystal separation rate of 200 lb/hr was achieved when the $(NH_4)_2SO_4$ solids in the feed to the centrifuge was 10% and the feed rate was 9 gpm. The moisture content of the product crystals was 3%. The screen bowl would be blinded by "mud" when the solids content of the feed decreased to 5%. Varying the g-force had little effect on the centrifuge performance.

### Piping Materials

Type 304 and 316 SS pipe and rubber hoses provided excellent service in piping ammoniacal liquors. Rubber hose was used in all corrosive material handling applications (prewash liquor and acidulator-stripper liquor and gas effluent streams) and was maintenance free. The connectors for the hoses were Kam-Loc fittings, a type of quick connect fitting. Metal Kam-Locs (SS and black iron) failed in corrosive liquor streams. Polypropylene fittings were corrosion resistant but had poor impact strength.

## INSTRUMENTATION

### Gas Flow Rate Measurement

The gas flow rate through the pilot plant was measured with a 8-1/2-in. I.D. sharp-edged orifice mounted in the ductwork downstream from the absorber. A Foxboro differential pressure (d/p) cell used to sense the pressure differential across the orifice did not perform reliably. Pressure taps led from the orifice to manometers mounted in the plant and control room. The orifice was calibrated and the gas flow determined from a graph. The orifice gave reliable service with only occasional cleaning of the pressure taps and manometer leads.

### Flowmeters for Liquid Flow Measurements

Foxboro magnetic flowmeters (Figure D-13) were used in measuring the flow rates of the following streams:

- Recirculating liquor to the absorber stages
- Absorber product bleedoff
- Humidification water to the prewash
- Forward feed water to the fourth-stage feed tank
- Absorber product liquor to the acidulator
- Forward feed to the evaporator-crystallizer

All of these units gave reliable service. A magnetic flowmeter used to measure the recirculating prewash sump liquor (pH = 1.0) failed. The type 316 SS electrode was eaten away, which allowed the corrosive liquor to penetrate the internals of the metering tube. The unit was replaced with one containing a platinum--10% iridium electrode to withstand highly corrosive liquids. The forward feed (water) magnetic flowmeters along with the absorber product flowmeter were coupled with flow integrators for detailed accounting of the flows.

### Process Recorders and Controllers

Foxboro electronic flow recording and controlling instruments were used in the pilot plant. The instruments were mounted in shelf units installed in the control board as shown in Figure D-14. The shelf units contained wiring terminal boards to which the instrument and the field-mounted flowmeters were connected. The electronic instruments were reliable and required no maintenance over a 3-yr period. The data recorded on the strip chart were easily read and provided quick access to past operating conditions. The 12-point temperature recorders, also from Foxboro, were satisfactory. The only maintenance required was an occasional cleaning of the slide-wires. Each motor had both a board-mounted and field-mounted control station. No problems were encountered with the Cutler-Hammer magnetic starters used throughout the plant. Ammeters were used on all major motors as a check of the loading.

### Gas Analyzers for the Pilot Plant

A DuPont 460 analyzer was used to monitor $SO_2$ in the plant gas streams. The analyzer was equipped with an automatic zero

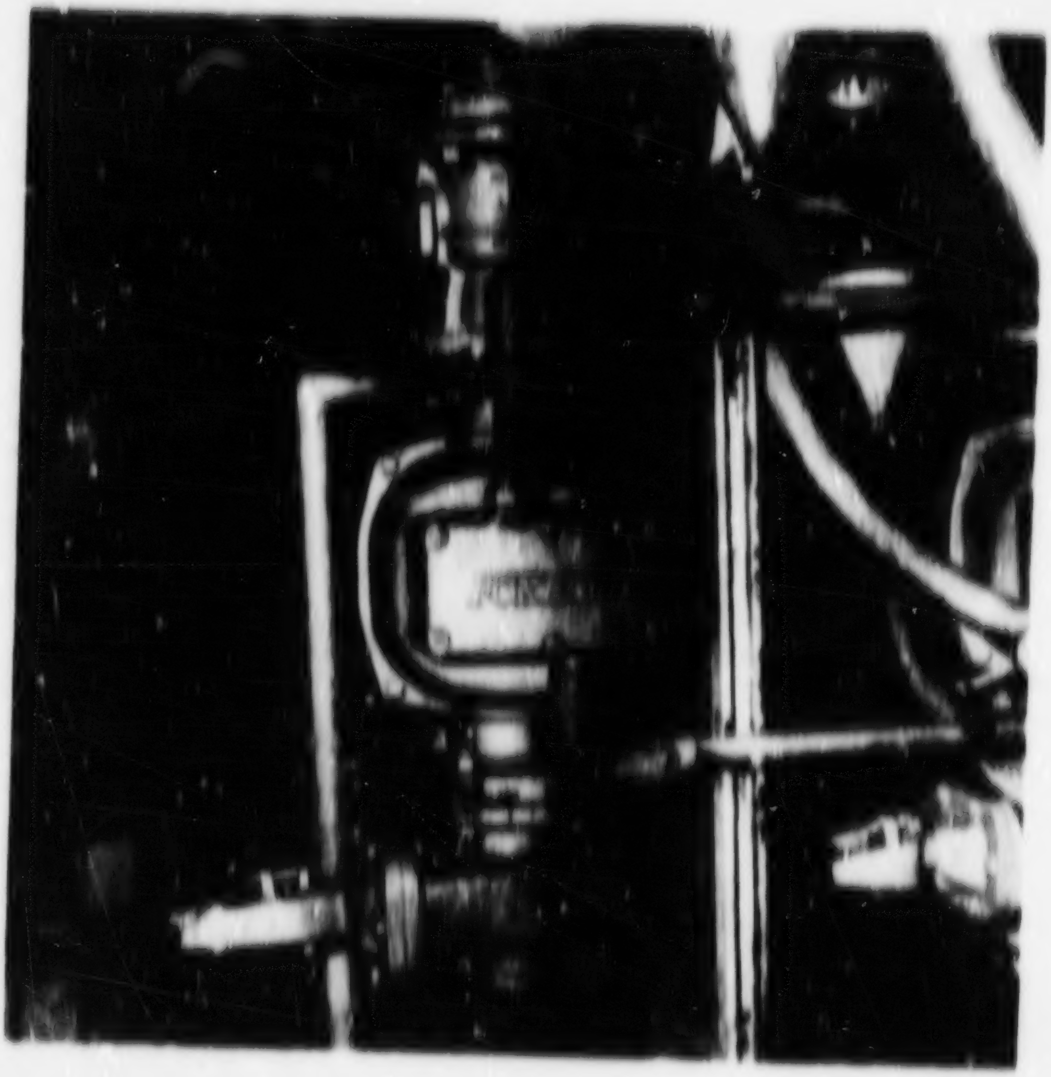

Figure D-13. Typical Foxboro magnetic flowmeter.

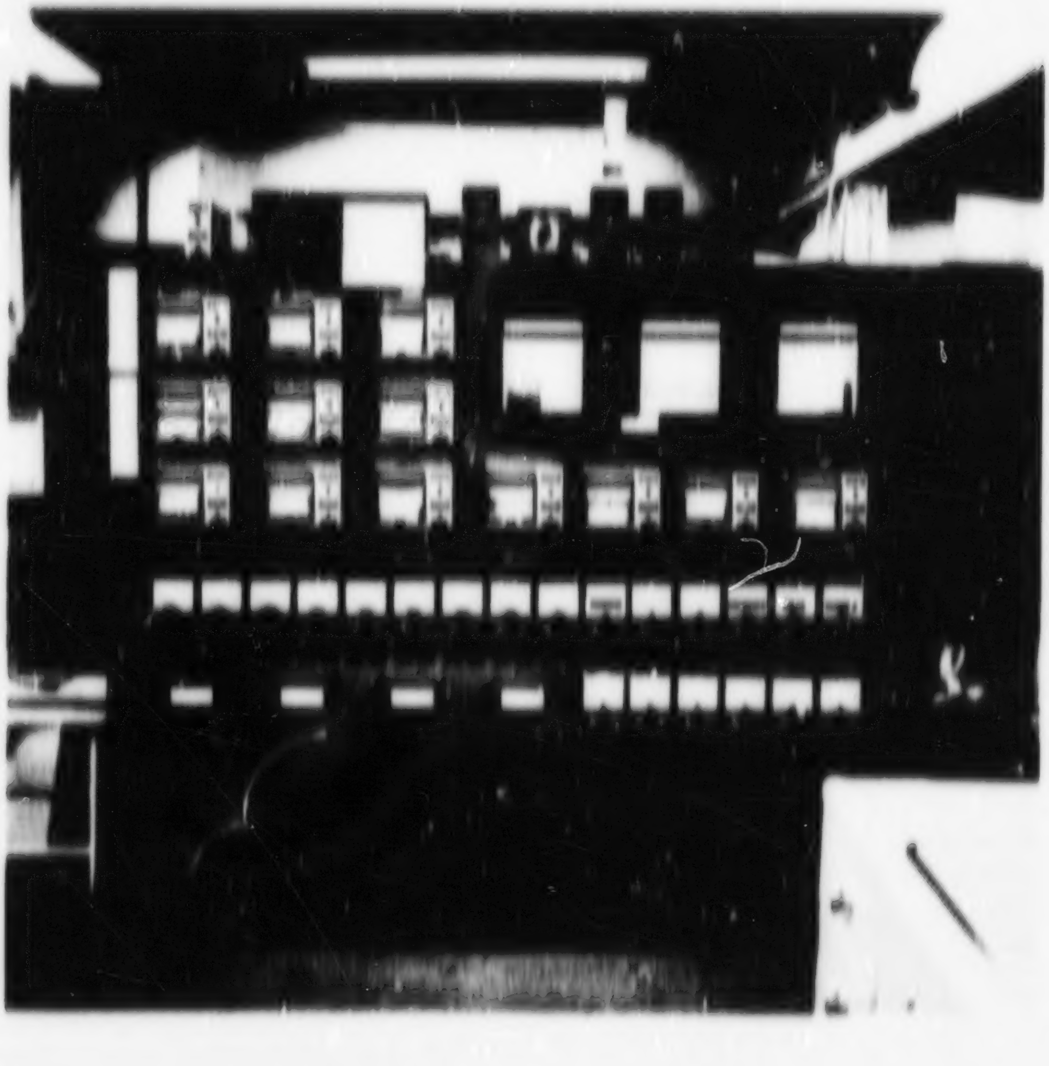

Figure D-14. Pilot-plant control board.

sequence, but the automatic sequence was bypassed and the instrument zeroed manually. Sample stations also were manually selected. The unit gave acceptable service. The prime maintenance area was keeping clean the sample lines and the light path in the measuring tube clean.

Stack opacity was measured in Ringlemann numbers with a Photomation Smoke Monitor. The instrument had a photocell to measure light transmittance from a single source through the plume. Initially, the unit performance was acceptable. Readout agreed with observations of trained visual emission observers. The lens faces required frequent cleaning. During the later test runs, the unit failed to zero and readings were taken by visual observers only.

# APPENDIX E

# FUME FORMATION IN AMMONIA SCRUBBERS

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# FUME FORMATION IN AMMONIA SCRUBBERS

## ABSTRACT

The published thermodynamic equations for the gas phase reaction of sulfur dioxide, ammonia, and water are reviewed and revised. The formation of a fume is predicted based upon the revised equations and compared to actual fuming conditions. The ammonia salt most likely to be formed is identified as ammonium sulfite monohydrate.

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# FUME FORMATION IN AMMONIA SCRUBBERS

## Introduction

Ammonia scrubbing has been employed for many years to remove sulfur dioxide from waste gases. With the recent enactment of the Clean Air Act, several processes using ammonia scrubbing have been proposed which produce a saleable byproduct from the ammonia scrubbing process. These products are elemental sulfur, sulfuric acid, and ammonium sulfate. Considerable pilot plant work on one of these processes has been carried out by the Tennessee Valley Authority.(1)

Ammonia scrubbing investigations, such as TVA's pilot plant investigations, have resulted in defining a problem of ammonia salt formation (fuming) as reported in Reference 1. Several other organizations have also reported this problem. A recent patent(2) issued to Air Products, Inc. deals specifically with this situation and claims certain techniques for controlling the formation of the fume. In this patent there are thermodynamic equations relating the concentrations of sulfur dioxide, ammonia, and water, and temperature to equilibrium constants. Previous work by Hillary St. Clair,(3) reviewed by Jonathan Earhart(4) also contains thermodynamic equations for the same ammonia salts as Air Products, Inc. has investigated.

An analysis and comparison of the available information was conducted to gain an understanding of the phenomenon of fume formation and to attempt to resolve differences in analyses which have been published.

## Background

Basically a gas phase reaction will produce a solid whenever the product of the partial pressures of the gases involved exceed the equilibrium constant for the reaction. The equilibrium constant for a reaction can be related to the heat of reaction as follows:

$$\frac{d\ (\log_e K)}{d(T)} = \frac{\Delta H}{RT^2} \qquad (1)$$

where $\Delta H$ = heat of reaction (calories/gram/mol)
$R$ = gas constant $\cong$ 1.987 (calories/gram/mol/°K)
$T$ = temperature (°K)

An alternate expression which is equivalent is

$$\frac{d\ (\log_{10} K)}{d\ (1/T)} = \frac{-\Delta H}{(\log_e 10)R} \qquad (2)$$

Assuming that $\Delta H$ is constant, integration of equation (2) gives

$$\log_{10} k = \frac{-\Delta H}{TR \log_e 10} + A \qquad (3)$$

The above form is used in all the calculations in this paper.

The heats of formation for $(NH_4)_2SO_3(s)$, $NH_4HSO_3(s)$ and $(NH_4)_2SO_3 \cdot H_2O(s)$ are published in "Circular of National Bureau of Standard 500, Selected Values of Chemical Thermodynamic Properties" issued February 1, 1952. The heat of formation of $(NH_4)_2S_2O_5(s)$ was not published by the Bureau of Standards. Air Products, Inc.(2) and St. Clair(3) report two different values for the heat of reaction for $(NH_4)_2S_2O_5(s) \rightarrow 2NH_3(g) + 2SO_2(g) + H_2O(g)$. Earhart(4) did not change the heat of reaction reported by St. Clair.

However, in his analysis Earhart did revise some of St. Clair's equations. These revisions were based upon the heat of formation of ammonium bisulfite which apparently was not available when St. Clair did his analysis in 1937. Table 1 is a comparison of Air Products thermodynamic equations and St. Clair's equations as changed by Earhart. Appendix I contains the calculations necessary to arrive at the values in Table 1.

TABLE 1. THERMODYNAMIC EQUATIONS

| Reaction | | Source | |
|---|---|---|---|
| | | St.Clair/Earhart | Air Products |
| $(NH_4)_2S_2O_5 \rightleftarrows 2NH_3+2SO_2+H_2O$ | $\log k_1$* | $-17050/T+41.26$ | $-16611/T+39.20$ |
| $NH_4HSO_3 \rightleftarrows NH_3+SO_2+H_2O$ | $\log k_2$ | $-9620/T+23.42$ | $-9611/T+22.76$ |
| $(NH_4)_2SO_3 \cdot H_2O \rightleftarrows 2NH_3+SO_2+2H_2O$ | $\log k_3$ | $-16520/T+43.73$ | $-15556/T+39.80$ |
| $(NH_4)_2SO_3 \rightleftarrows 2NH_3+SO_2+H_2O$ | $\log k_4$ | $-13370/T+32.26$ | $-13500/T+32.08$ |

*T = temperature (°R), k = atm$^5$

An examination of Table 1 shows some differences and some marked similarities. An investigation and analysis of the available data was conducted in an attempt to resolve the differences. If a resolution could be obtained, then a comparison of the resolution to known conditions for fume formation would be conducted.

## Analysis

The first question or difference to be reviewed was what is the value to assume for heat of reaction for the following:

$$(NH_4)_2S_2O_5(S) \rightleftarrows 2NH_3(g) + 2SO_2(g) + H_2O\ (g)$$

$$\log_{10}k = \frac{-\Delta H}{(\log_e 10)RT} + A$$

St. Clair reported 78 kcal and Air Products, Inc. reported 76 kcal for this value. A least squares analysis of St. Clair's data performed by the author showed 76 kcal as the value (Appendix II). However, the value of 78 kcal could not be rejected based on the analysis of Appendix II. Therefore, a second approach, namely determining a lower bound for the heat of reaction, as shown in Appendix III rejected a ΔH less than 76.45 kcal. Therefore it was assumed that a ΔH of 78 kcal was appropriate and Air Products and the least squares analysis ΔH values were not used. The second step was to define the value of the constant, A, since a difference exists in the published material. To accept St. Clair's value for the constant would lead to the same equations as Earhart obtained. Air Products value appeared questionable since the heat of reaction was in error, yet Air Products value could not be rejected based on the analysis contained in Appendix II. So, an independent method was used based on other data(5), namely the solubility diagram for the system $NH_3$-$SO_2$-$SO_3$-$H_2O$. The details of the method and results are contained in Appendix IV. The results showed that Air Products constant is valid. Table 2 is a compilation of Table 1 and the thermodynamic equations developed from Appendix IV.

## Application

Consider the following reactions:

$$NH_4HSO_3 \rightleftarrows NH_3 + SO_2 + H_2O$$

$$\log k_2 = -9611/T + 31.28$$

$$(NH_4)_2SO_3 \cdot H_2O \rightleftarrows 2NH_3 + SO_2 + 2H_2O$$

$$\log k_3 = -16556/T + 58.204$$

TABLE 2

| Reaction | Source<br>St. Clair/Barker* | Air Products | Author |
|---|---|---|---|
| 1. $(NH_4)_2S_2O_5(s) \rightarrow 2NH_3(g) + 2SO_2(g) + H_2O(g)$ | log K = −17850/T+41.26 | −18611/T+39.23 | −17850/T+39.21 |
| 2. $NH_4HSO_3(s) \rightarrow NH_3(g) + SO_2(g) + H_2O(g)$ | log K = −9620/T+23.42 | −9611/T+22.76 | −9620/T+22.76 |
| 3. $(NH_4)_2SO_3 \cdot H_2O(s) \rightarrow 2NH_3(g) + SO_2(g) + 2H_2O(g)$ | log K = −18520/T+40.73 | −18556/T+39.80 | −18520/T+39.33 |
| 4. $(NH_4)_2SO_3(s) \rightarrow 2NH_3(g) + SO_2(g) + H_2O(g)$ | log K = −13370/T+32.29 | −13560/T+32.28 | −13368/T+31.62 |

ADDITIONAL EQUILIBRIUM CONSTANTS

| Reaction | |
|---|---|
| (a) $2NH_4HSO_3(s) \rightarrow (NH_4)_2S_2O_5(s) + H_2O(g)$ | log K = −2290/T+6.11 |
| (b) $(NH_4)_2S_2O_5(s) \rightarrow (NH_4)_2SO_3(s) + SO_2(g)$ | log K = −2681/T 6.59 |
| (c) $(NH_4)_2SO_3 \cdot H_2O(s) \rightarrow (NH_4)_2SO_3(s) + H_2O(g)$ | log K = −3151/T+8.46 |
| (d) $2NH_4HSO_3(s) \rightarrow (NH_4)_2SO_3 \cdot H_2O(s) + SO_2(g)$ | logK = −2720/T+6.21 |

*Logarithms are to the base 10, equilibrium constants are in atmospheres.
T = temperature (degrees Kelvin)

These are two of the reactions with the associated equilibrium constants which are published in Air Products patent. The question now arises as to whether one could operate a scrubber as outlined in Air Products patent and still fume.

Assume that we have isothermal operation (125°F), a prescrubber to humidify the gas and remove HCl and a three stage scrubber with the compositions on each stage as shown in Figure 1.

$$\log k_2\ (324.82°K) = 1.6513 \qquad k_2 = 44.80\ \text{atm}^3$$

$$\log k_3\ (324.82°K) = 3.234 \qquad k_3 = 1714.87\ \text{atm}^3$$

From this typical example, one can observe that at no point in the scrubber is the product of $P_{H_2O} \cdot P_{NH_3} \cdot P_{SO_2}$ in violation of Air Products' equation for ammonium bisulfite; however, using the ammonium sulfite monohydrate equations, one would predict a fume. It is interesting to note that at approximately 125°F, the patent does not contain any experimental work above approximately 73 mm $H_2O$. Therefore, although one may concede that the fume formed in Air Products work was indeed the bisulfite, extrapolation of the work to actual scrubber conditions, as shown in Figure 1 would indicate that the patent is not operable. The equations developed in this paper are even more critical than Air Products with respect to the formation of ammonium sulfite monohydrate. Appendix V shows the typical scrubber conditions employed at TVA's Colbert pilot plant, the point of fume formation and the recommended method for avoiding a fume using the equations developed here. Reference 1 confirms that the fume is formed under conditions very similar to those depicted in Figure 1.

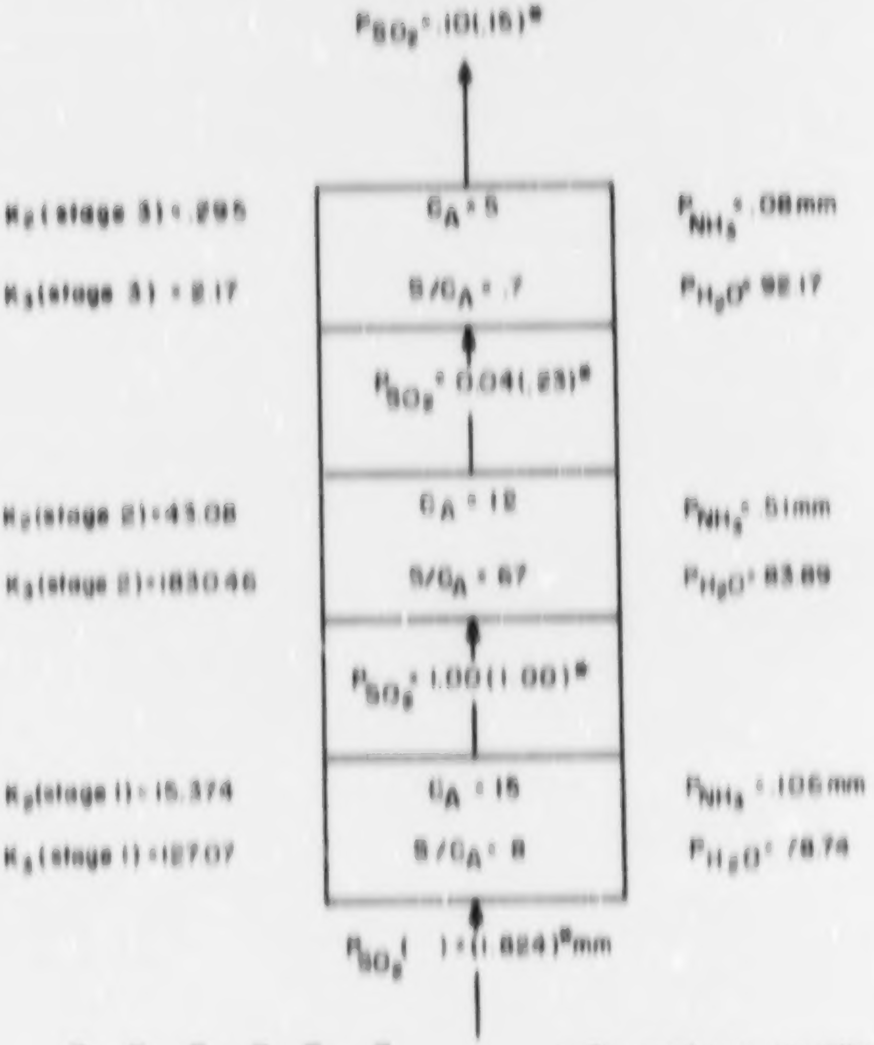
## Conclusions

For the scrubbing conditions employed at TVA's Colbert pilot plant, a fume can form under isothermal operations, and with a prewash section. The fume is most likely ammonium sulfite monohydrate and not ammonium bisulfite.

Operation of a scrubber as proposed in Air Products patent may not prevent the formation of a fume.

Further pilot plant testing is needed to define regions of fume-free operation.

Figure I Comparison of K2 and K3 values for liquors in three-stage absorber operation.


$P_{SO_2}$ = .10(.15)*
$K_2$ (stage 3) = .295
$K_3$ (stage 3) = 2.17
$C_A$ = 5
$S/C_A$ = .7
$P_{NH_3}$ = .08 mm
$P_{H_2O}$ = 92.17
$P_{SO_2}$ = 0.04(.23)*
$K_2$ (stage 2) = 43.08
$K_3$ (stage 2) = 1830.46
$C_A$ = 12
$S/C_A$ = .87
$P_{NH_3}$ = .51 mm
$P_{H_2O}$ = 83.89
$P_{SO_2}$ = 1.00(1.00)*
$K_2$ (stage 1) = 15.374
$K_3$ (stage 1) = 127.07
$C_A$ = 15
$S/C_A$ = .8
$P_{NH_3}$ = .106 mm
$P_{H_2O}$ = 78.74
$P_{SO_2}$ (   ) = (1.824)* mm

$$K_2 = \left[P_{SO_2}\right] \left[P_{NH_3}\right] \left[P_{H_2O}\right]$$

$$K_3 \left[P_{SO_2}\right] \left[P_{NH_3}\right]^2 \left[P_{H_2O}\right]^2$$

* The number in parenthesis is the typical concentration obtained in TVA's pilot plant

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## APPENDIX I

## CALCULATIONS FOR COMPARING THERMODYNAMIC EQUATIONS

Air Products equations(2) are as follows:

$1/2(NH_4)_2S_2O_5 \rightleftharpoons NH_3 + SO_2 + 1/2H_2O$

$\log_{10}K_1 = (-14,950/T) + 26.8$

$NH_4HSO_3 \rightleftharpoons NH_3 + H_2O + SO_2$

$\log_{10}K_2 = (-17,300/T) + 31.4$

$1/2(NH_4)_2SO_3 \cdot H_2O \rightleftharpoons NH_3 + H_2O + 1/2SO_2$

$\log_{10}K_3 = (-14,900/T) + 27.1$

$(NH_4)_2SO_3 \rightleftharpoons 2NH_3 + SO_2 + H_2O$

$\log_{10}K_4 = (-24,300/T) + 43.6$

The temperature T is in degrees Rankine and the partial pressures are in millimeters of mercury. To convert to degrees K and atmospheres the following equations were used.

$T(°K) = 5/9\ T\ (°R)$

$\log_{10}$ (760 mm = 1 atmosphere) = 2.8808

Also the equations for ammonium pyrosulfite and ammonium sulfite monohydrate are multiplied by two in order to place all equations on a mol basis for the salt. Applying these transformations to Air Products equations, the following are obtained.

$\log_{10}K_1 = -16611/T + 39.196$

$\log_{10}K_2 = -9611/T + 22.758$

$\log_{10}K_3 = -16555/T + 39.796$

$\log_{10}K_4 = -13500/T + 32.077$

Earharts' corrections(4) to St. Clair's data led to the following equations.

$(NH_4)_2S_2O_5 \rightarrow 2NH_3 + 2SO_2 + H_2O$ (1)

$\log k_1 = -17050/T + 41.255$

$2NH_4HSO_3 \rightarrow (NH_4)_2S_2O_5 + H_2O$ (a)

$\log k_a = -2190/T + 5.578$

$(NH_4)_2S_2O_5 \rightarrow (NH_4)_2SO_3 + SO_2$ (b)

$\log k_b = -3680/T + 8.997$

$(NH_4)_2SO_3 \cdot H_2O \rightarrow (NH_4)_2SO_3 + H_2O$ (c)

$\log k_c = -3150/T + 8.476$

T, in this case, is in degrees Kelvin and partial pressures are in atmospheres. Combining equations (1) and (a), (1) and (b), (c) and (1) and (b) the following was obtained.

$NH_4HSO_3 \rightleftarrows NH_3 + SO_2 + H_2O$

$\log k_2 = -9620/T + 23.4165$

$(NH_4)_2SO_3 \cdot H_2O \rightleftarrows 2NH_3 + 2H_2O + SO_2$

$\log k_3 = -16520/T + 40.738$

$(NH_4)_2SO_3 \rightleftarrows 2NH_3 + SO_2 + H_2O$

$\log k_4 = -13370/T + 32.258$

## APPENDIX II

## ANALYSIS OF DATA PUBLISHED BY HILLARY ST. CLAIR(3)

| Temperature °C | °K | W grams/liter | P atmospheres | $Y = \log_{10}P$ | $X = \frac{1000}{T(°K)}$ |
|---|---|---|---|---|---|
| 60 | 333.15 | 0.048 | 0.030 | -1.5229 | 3.00165 |
| 70 | 343.15 | 0.102 | 0.070 | -1.1549 | 2.91418 |
| 80 | 353.15 | 0.158 | 0.108 | - .9666 | 2.83166 |
| 90 | 363.15 | 0.295 | 0.204 | - .6904 | 2.75368 |
| 100 | 373.15 | 0.534 | 0.365 | - .4377 | 2.67989 |
| 110 | 383.15 | 0.986 | 0.646 | - .1898 | 2.60994 |

$$\log_{10}P = \frac{-\Delta H}{T(1.987)(\log_e 10)(5)} + C$$

$$\log_{10}K = 5\log_{10}P + \log(16/3125)$$

$$\Sigma x^2 = 47.097 \quad \Sigma y^2 = 5.29144 \quad \Sigma x = 16.791 \quad \Sigma y = -4.9622$$

$$\begin{bmatrix} x^Tx \end{bmatrix} = \begin{bmatrix} 6 & 16.791 \\ 16.791 & 47.097 \end{bmatrix} \qquad \begin{bmatrix} x^Tx \end{bmatrix}^{-1} = \begin{bmatrix} \dfrac{\begin{matrix} 47.097 & -16.791 \\ -16.791 & 6 \end{matrix}}{0.644316} \end{bmatrix}$$

$$\begin{bmatrix} x^Ty \end{bmatrix} = \begin{bmatrix} -4.9622 \\ -14.2431 \end{bmatrix} \qquad B = \begin{bmatrix} x^Tx \end{bmatrix}^{-1} \begin{bmatrix} x^Ty \end{bmatrix} = \begin{bmatrix} 8.4603 \\ -3.3167 \end{bmatrix}$$

$$\log_{10}P = -3316.7/T + 8.46$$

$$\log_{10}K = -16583.5/T + 40.01$$

### Analysis of Variance

| Source | Sum of Squares | Degrees of Freedom | Mean Square | F-Ratio |
|---|---|---|---|---|
| Mean ($b_0$) | 4.1039 | 1 | | |
| x ($b_1$) | 1.1830 | 1 | 1.1830 | 1075 |
| Residual | .0045 | 4 | .0011 | $\hat{\sigma}^2$ |
| Total | 5.2914 | 6 | | |

$$\mathrm{Var}(b_0) = \hat{\sigma}^2 \left( \frac{\Sigma x^2}{n\Sigma x^2 - (\Sigma x)^2} \right) = .3289$$

$$\mathrm{Var}(b_1) = \hat{\sigma}^2 \left( \frac{n}{n\Sigma x^2 - (\Sigma x)^2} \right) = .0419$$

# APPENDIX III

## BOUNDARY FOR HEAT OF FORMATION OF AMMONIUM PYROSULFITE

Consider the following reactions

$$(NH_4)_2S_2O_5(s) \rightarrow 2NH_3(g) + 2\ SO_2(g) + H_2O(g) \qquad (1)$$

$$(NH_4)_2S_2O_5(s) \rightarrow (NH_4)_2SO_3(s) + SO_2(g) \qquad (2)$$

$$\Delta H_1(\text{kcal}) = 2(-11.04) + 2(-70.96) - 57.80 - \Delta H_{(NH_4)_2S_2O_5}$$

$$\Delta H_2(\text{kcal}) = -212.0 - 70.96 - \Delta H_{(NH_4)_2S_2O_5}$$

Assuming that the heats of formation are constant, then

$$\log_{10}K_1 = \frac{-\Delta H_1\ (1000)}{T(\log_e 10)(1.987)} + a$$

$$\log_{10}K_2 = \frac{-\Delta H_2\ (1000)}{T(\log_e 10)(1.987)} + b$$

$$\Delta H_1 = -221.8 - \Delta H \qquad (3)$$

$$\Delta H_2 = -282.96 - \Delta H \qquad (4)$$

$$K_1 = \left[P_{NH_3}\right]^2 \left[P_{SO_2}\right]^2 \left[P_{H_2O}\right] \qquad (5)$$

$$\left[P_{NH_3}\right] = \left[P_{SO_2}\right] \qquad \left[P_{H_2O}\right] = \left[1/2 P_{SO_2}\right]$$

Substituting the above in equation 5, we obtain an expression for the vapor pressure of $SO_2$ due to $(NH_4)_2S_2O_5$ decomposition

$$K_1 = 1/2\left[\hat{P}_{SO_2}\right]^5$$

$$\log \hat{P}_{SO_2} = 1/5 \log K_1 + 1/5 \log 2 \qquad (6)$$

$$\log \hat{P}_{SO_2} = 1/5\left[\frac{-\Delta H_1 \cdot 1000 + a}{T \cdot \log_e 10 \cdot 1.987}\right] + 1/5 \log 2 \qquad (7)$$

Similarly the following expression represents the vapor pressure of $SO_2$ due to reaction (2)

$$\log P_{SO_2} = \frac{-\Delta H_2 \cdot 1000}{T \cdot \log_e 10 \cdot 1.987} + b \qquad (8)$$

Now at some temperature, say $\hat{T}$, there will be an equilibrium such that $\log P_{SO_2} = \log \hat{P}_{SO_2}$. St. Clair in reference 1 cites 120°C as very nearly this temperature. For the moment let's not specify the exact temperature other than to agree that one exists. What we wish to do is to establish a $\Delta H$ for $(NH_4)_2S_2O_5$ such that for some temperature T greater than $\hat{T}$, $(NH_4)_2SO_3(S)$ will be the stable compound and for a temperature less than $\hat{T}$ $(NH_4)_2S_2O_5(S)$ will be the stable compound.

Combining equations 3, 4, 7, 8 we obtain

$$\log \hat{P}_{SO_2} - \log P_{SO_2} = a^*\left[\frac{-\Delta H_1}{5T}\right] + \frac{a}{5} + 1/5 \log 2 \qquad (9)$$

$$+ a\left[\frac{\Delta H_2}{T}\right] - b$$

$$\log \hat{P}_{SO_2} - \log P_{SO_2} = a\left[\frac{\Delta H_2}{T} - \frac{\Delta H_1}{5T}\right] + a/5 + 1/5 \log_2 - b$$

$$= a\left[\frac{-238.6 - .8\Delta H}{T}\right] + a/5 + 1/5 \log_2 - b$$

$$a/5 + 1/5 \log_2 - b = a\left[\frac{+.8\Delta H + 238.6}{\hat{T}}\right] \text{ since}$$

$$\log \hat{P}_{SO_2} - \log P_{SO_2} = 0 \text{ for } T = \hat{T}$$

$$\text{Now } \log \hat{P}_{SO_2} - \log P_{SO_2} = - a/T\,[238.6 + .8\Delta H]$$

$$+ a/\hat{T}\,[238.6 + .8\Delta H]$$

For $T < \hat{T}$ $\log \hat{P}_{SO_2} > \log P_{SO_2}$; therefore

$$-\frac{(238.6 + .8\Delta H)}{T} > -\frac{(238.6 + .8\Delta H)}{\hat{T}}$$

$$\frac{(238.6 + .8\Delta H)}{T} < \frac{(238.6 + .8\Delta H)}{\hat{T}}$$

---

$^*a = \frac{1000}{(\log_e 10)(1.987)}$

For the inequality to hold with $T < \hat{T}$, the expression $238.6 + .8\Delta H$ must be negative.

Therefore, $238.6 + .8\Delta H < 0 \Rightarrow \Delta H_{(NH_4)_2S_2O_8} < -298.25$ kcal

Hence, $\Delta H_1 > 76.45$, $\log k_1 < -16709.52/T + a$, and

$\log k_2 < -3341.9/T + b$ for any a and b.

# APPENDIX IV

## CALCULATIONS OF EQUILIBRIUM CONSTANTS

Based upon the results of Appendices 1 and 2 and the uncertainty of the intercept for the reaction

$$(NH_4)_2S_2O_5(s) \rightleftarrows 2NH_3(g) + 2SO_2(g) + H_2O(g) \qquad (1)$$

It was decided to assume that ΔH for reaction 1 was 78,000 calories and solve for A in the following equation

$$\log_{10}K_1 = -17050/T + A$$

Table 1 is a list of the reactions to be considered. Reference 5 contains the solubility diagram for the system $NH_3$-$SO_2$-$SO_3$ at 86°F (Figure 13 - page 33 of reference 5).

Using this diagram in conjunction with Johnstone's equations for the vapor pressure of $NH_3$, $SO_2$ and $H_2O$ we can calculate

$K_2 = \left[P_{NH_3}\right]^2 \left[P_{SO_2}\right]\left[P_{H_2O}\right]^2$ for various $C_A$'s and $S/C_A$'s and solve for $\log k_2 = -16520/T + C$ for the reaction

$$(NH_4)_2SO_3 \cdot H_2O(s) \rightleftarrows 2NH_3(g) + 2H_2O(g) + SO_2(g) \, (2)$$

At $C_A = 45$ the saturation line for $(NH_4)_2SO_3 \cdot H_2O$ with no ammonium sulfate present gives $S/C_A = .87$. Using Johnstone's equation $K_2$ for $C_A = 45$ $S/C_A = .87$ is calculated as follows:

$$K_2 = \left[P_{NH_3}\right]^2 \left[P_{SO_2}\right] \left[P_{H_2O}\right]^2 = \frac{N^2M \cdot C_A^2(C_A-S)P_w^2(1.1001)^2}{(100 + C_a + S)^2}$$

Where N = .0017 M = .01123 for T = 303.15 °k

$\log k_2 = -16520/T + C$

For t = 86°F (303.15°k)

$\log k_2 = -54.49447 + C$

$$k_2 = \frac{3.285 \times 10^{-5}(C_a^2)(C_a - S)(P_w)^2}{(100 + C_a + S)^2}$$

$P_w$ at 303.15 = 31.824 mm

And

$C_a = 85 \quad S = 39.15$

$$k_3 = \frac{1.285 \times 10^{-5} (85)^2 (5.85)(31.878)^2}{(100 + 85 + 39.15)^2}$$

$k_3 = .1108$

$\log k_3 = -.9556 = -54.49447 + C$
$C = 53.5388$

$\log k_3 = -16520/T + 39.1$ for $k_3$ in atm$^5$

This value also for C does not exceed solubility at lower values of $C_a$. Again referring to Figure 13 of reference 5 the maximum solubility of $NH_4HSO_3$ is given at $C_a = 43$ and $S/C_a = .875$. Again applying Johnstone's equations to

$\log k_2 = -9620/T + B$

for $NH_4HSO_3(s) \rightleftarrows NH_3(g) + SO_2(g) + H_2O(g)$, we can solve for B as follows:

$$\left[p_{NH_3}\right]\left[p_{H_2O}\right]\left[p_{SO_2}\right] = \frac{N \cdot M \cdot C_a \cdot (2S - C_a) \cdot p_w (100)}{100 + C_a + S} = k_2$$

$$k_2 = \frac{1.9091 \times 10^{-5} (43)(32.25)(31.826)(100)}{100 + 43 + 37.625}$$

$$k_2 = \frac{8.4257 \times 10^{+1}}{180.625} = .4665$$

$\log k_2 = -.3312$

$B = 9620/T + \log k_2 = 31.4$

$B = 22.76$ for $k_2$ in atm$^3$

$\log k_2 = -9620/T + 22.76$

For the following reaction

$(NH_4)_2SO_3 \cdot H_2O(s) \rightleftarrows (NH_4)_2SO_3(s) + H_2O(g)$

St. Clair cited reference 7 which states that below 81°C the hydrated sulfite is in equilibrium with the saturated solution and above 81°C the anhydrous sulfite is in equilibrium. Using Earhart's calculations(3) which assumes 81°C to be the transition point, complete ionization of the salt and Raoult's law;

$\log_{10} P_{H_2O} = -3151/T + 8.48$

We are now in a position to calculate the equilibrium constant of equation 4 as follows:

$$\log k_4 = \log k_3 - \log_{10} P_{H_2O}$$
$$= -16520/T + 3151/T + 39.10 - 8.48$$

$$\log k_4 = -13369/T + 30.62$$

St. Clair also cited reference 8 as the source for which the vapor pressure of $SO_2$ from the decomposition of ammonium pyrosulfite at 120°C is equal to the partial pressure of $SO_2$ due to the following reaction:

$$(NH_4)_2S_2O_5(s) \rightleftarrows (NH_4)_2SO_3(s) + SO_2(g) \qquad (5)$$

$$\log k_5 = -3681/T + B = \log P_{SO_2}$$

The vapor pressure of $SO_2$ due to the decomposition at $(NH_4)_2S_2O_5$ is as follows:

$$(NH_4)_2S_2O_5 \rightleftarrows 2NH_3 + 2SO_2 + H_2O$$

$$k_1 = \left[P_{NH_3}\right]^2 \left[P_{SO_2}\right]^2 \left[P_{H_2O}\right]$$

$$P_{SO_2} = P_{NH_3},\ P_{H_2O} = 1/2\ P_{SO_2}$$

$$k_1 = \left[P_{SO_2}\right]^2 \left[P_{SO_2}\right]^2 \left[\frac{P_{SO_2}}{2}\right] = \frac{(P_{SO_2})^5}{2}$$

$$\log P_{SO_2} = 1/5 \log k_1 + 1/5 \log 2$$

$$\log P_{SO_2} = 1/5 \left[-17050/T + A\right] + 1/5 \log 2, \text{ at } T = 393.15°K$$

Also $\log k_5 = \log k_1 - \log k_4$, since

$$(NH_4)_2S_2O_5(s) \xrightleftharpoons[]{\log k_1} 2NH_3(g) + 2SO_2(g) + H_2O(g)$$

$$(NH_4)_2SO_3(s) \xrightleftharpoons[]{\log k_4} 2NH_3(g) + SO_2(g) + H_2O(g)$$

$$\log k_5 = -17050/T + A + 13369/T - 30.62$$

$$\log k_5 = -3681/T + B = -3681/T + A - 30.62$$

$$\text{or } B = A - 30.62 \text{ at } T = 393.15°K$$

$$\log k_5 = -3410/T + A/5 + 1/5 \log 2 = -3681/T + B$$

$$B = 271/T + A/5 + 1/5 \log 2$$

Combining, and solving these equations at T = 393.15

$E = A - 10.62$

$5E = 1355/T + A + \log 2$

$5A - 53.10 = 5E = 3.4465 + A + .3010$

$4A = 56.8475 \therefore A = 14.21, E = 3.59$

## TABLE OF REACTIONS

$(NH_4)_2S_2O_5(s) \rightleftarrows 2NH_3(g) + 2SO_2(g) + H_2O(g)$ (1)

$\log_{10}K_1 = -17050/T + A$

$NH_4HSO_3(s) \rightleftarrows NH_3(g) + SO_2(g) + H_2O(g)$ (2)

$\log_{10}K_2 = -9620/T + B$

$(NH_4)_2SO_3 \cdot H_2O(s) \rightleftarrows 2NH_3(g) + SO_2(g) + 2H_2O(g)$ (3)

$\log K_3 = -16520/T + C$

$(NH_4)_2SO_3(s) \rightleftarrows 2NH_3(g) + SO_2(g) + H_2O(g)$ (4)

$\log K_4 = -13369/T + D$

# APPENDIX V

## TYPICAL SCRUBBING STAGES
## AT TVA's COLBERT PILOT PLANT

The operation of the ammonia scrubbing pilot plant with a prewash section and a three-stage absorber has been typified by the following concentrations on each stage:

Stage 1 $C_A = 15$ $S/C_A = .8$ $T = 125°F$

Stage 2 $C_A = 12$ $S/C_A = .67$ $T = 125°F$

Stage 3 $C_A = 5$ $S/C_A = .7$ $T = 125°F$

Figures 1, 2, and 3 show the partial pressures of $SO_2$ versus 1/T for equilibrium and the partial pressures of $SO_2$ required to produce a fume assuming the fume is ammonium sulfite monohydrate and the equation for the reaction

$$(NH_4)_2SO_3 \cdot H_2O(s) \rightleftarrows 2NH_3(g) + SO_2(g) + 2H_2O(g)$$

is given by

$$\log k_p = -16520/T + 39.1$$

Examination of Figures 1, 2, and 3 point to the second stage of the absorber as the point of fume formation. This is consistent with observations by pilot plant personnel that the fume is observed around the second stage. Also the margin of safety on stages 1 and 3 point to altering the second stage composition as shown in Figure 4 to avoid a fume and the addition of a fourth stage (Figure 5) to achieve high $SO_2$ removal and low (less than 50 ppm) ammonia loss.

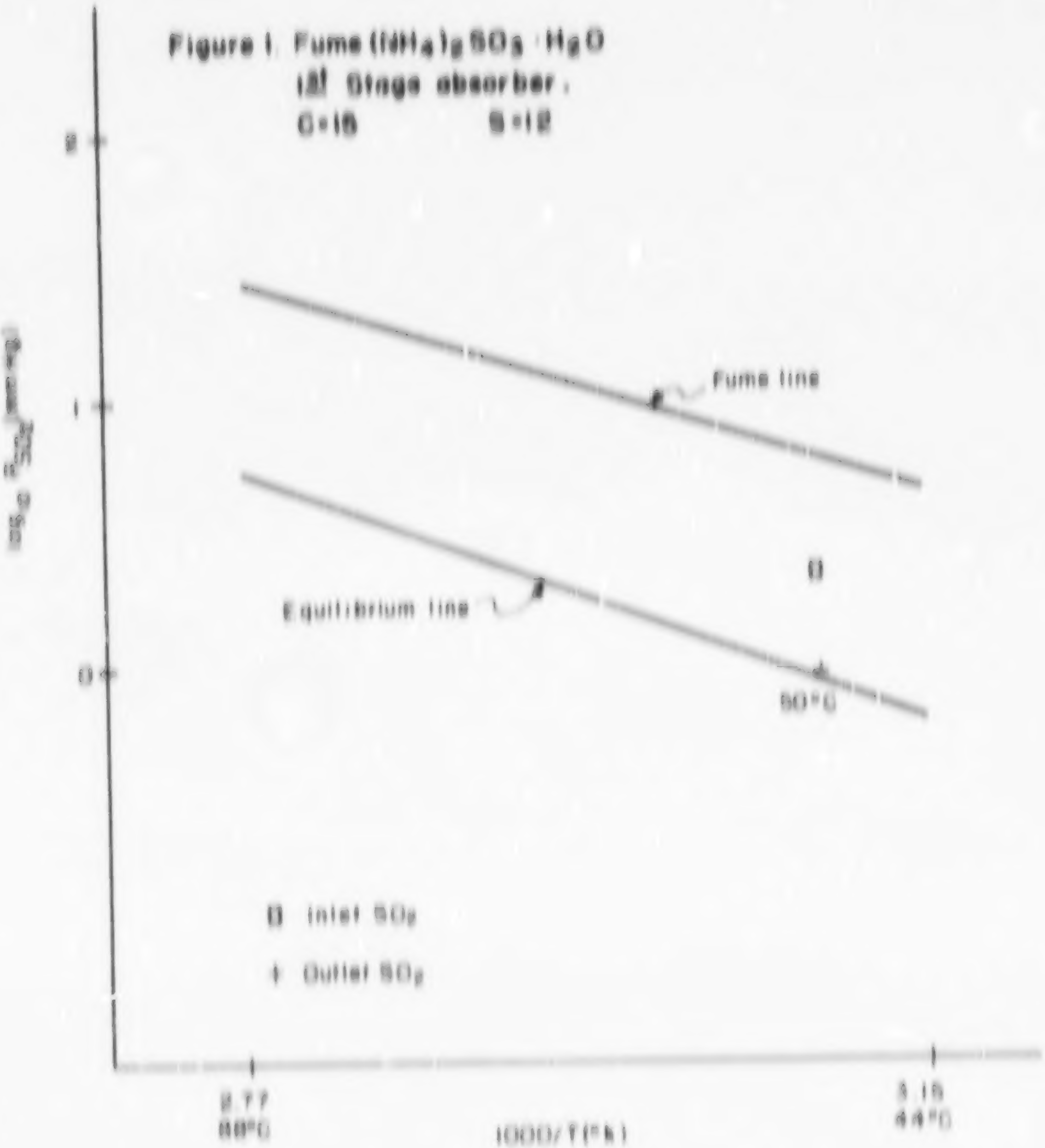

Figure 1. Fume (NH$_4$)$_2$SO$_3$ · H$_2$O
1st Stage absorber,
G=15 S=12

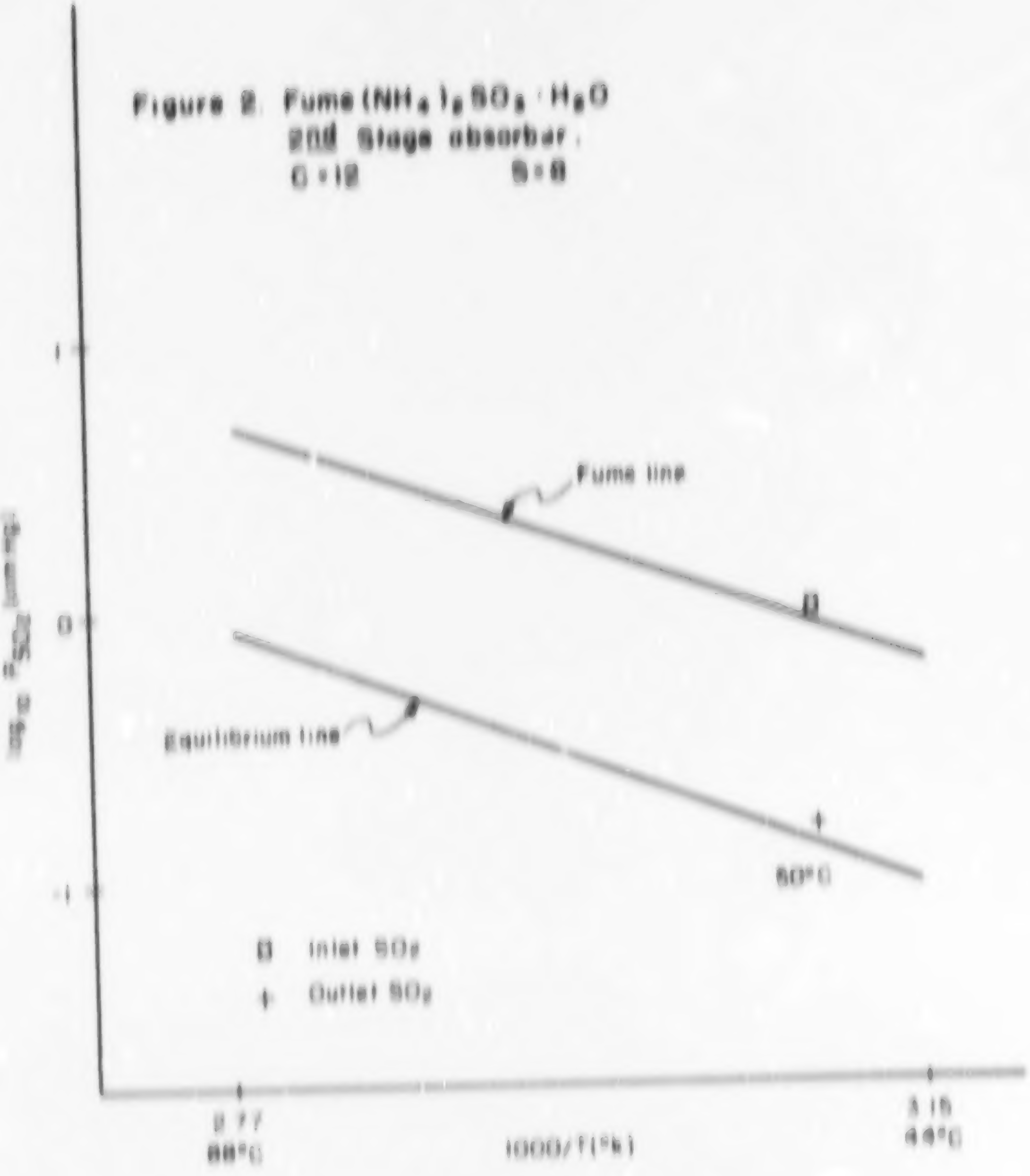

Figure 2. Fume $(NH_4)_2SO_3 \cdot H_2O$
2nd Stage absorber.
C = 12   S = 8

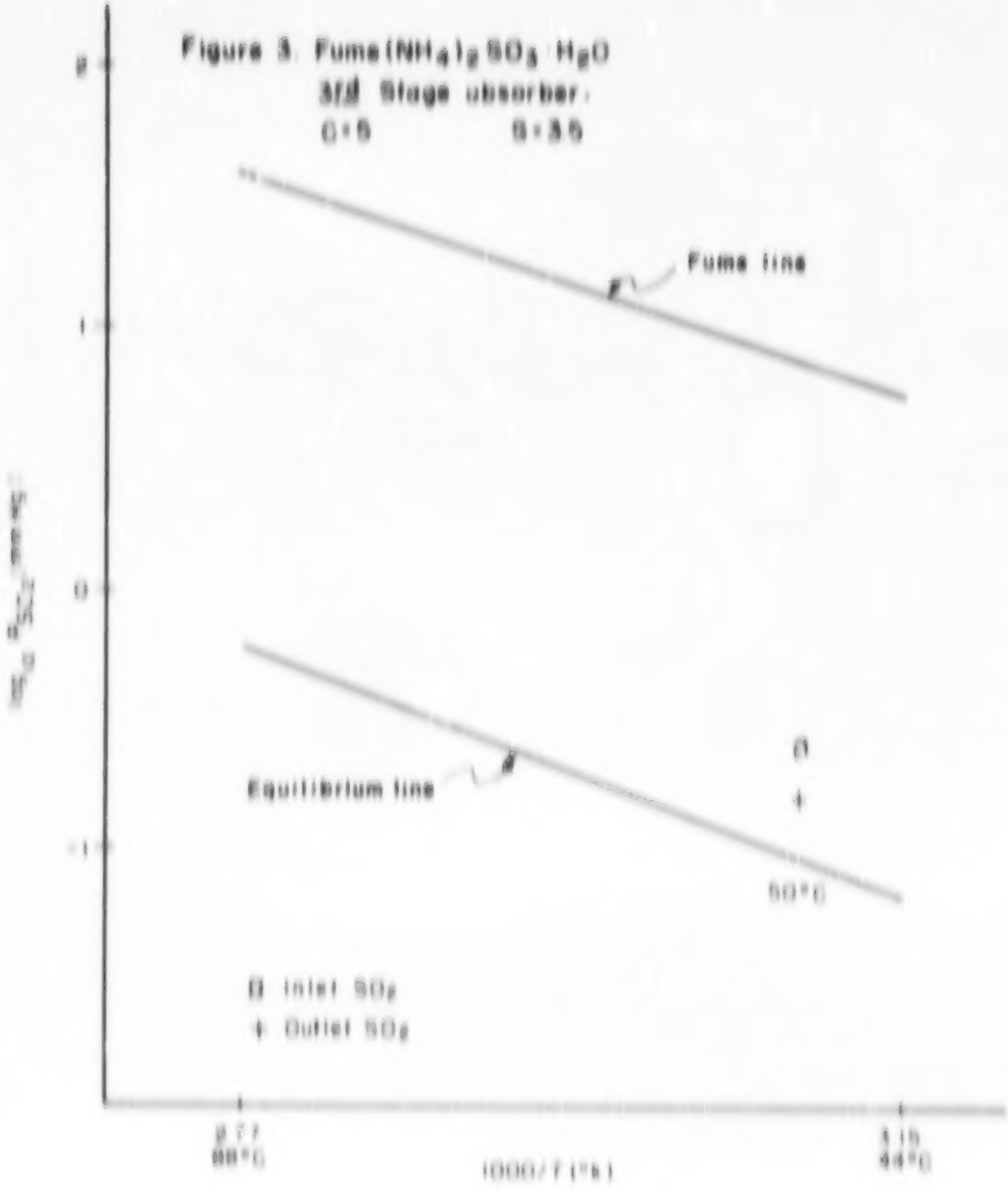

Figure 3. Fume $(NH_4)_2SO_3 \cdot H_2O$
3rd Stage absorber:
C=5 S=3.5

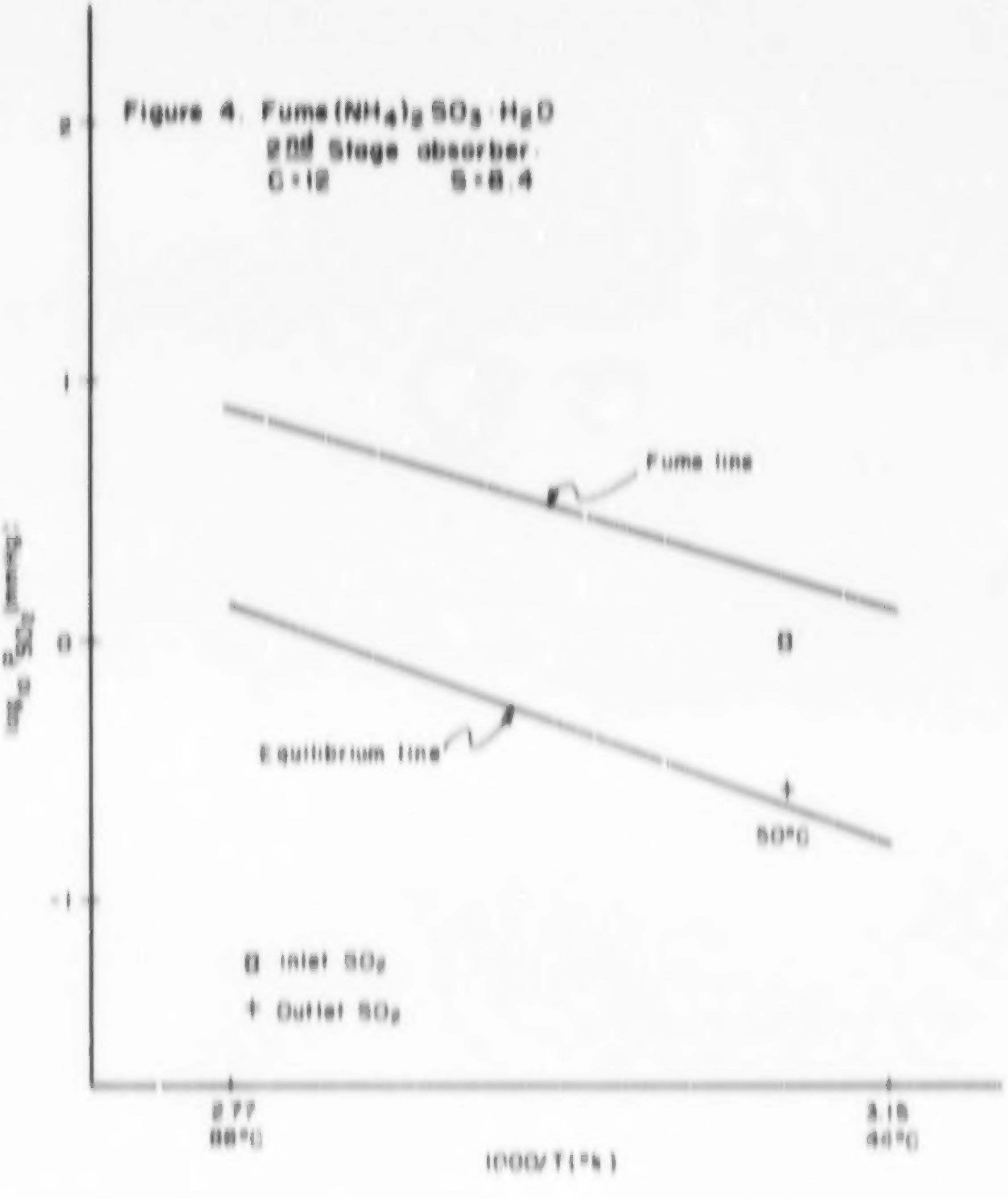

Figure 4. Fume $(NH_4)_2SO_3 \cdot H_2O$
2nd Stage absorber
C=12 S=8.4

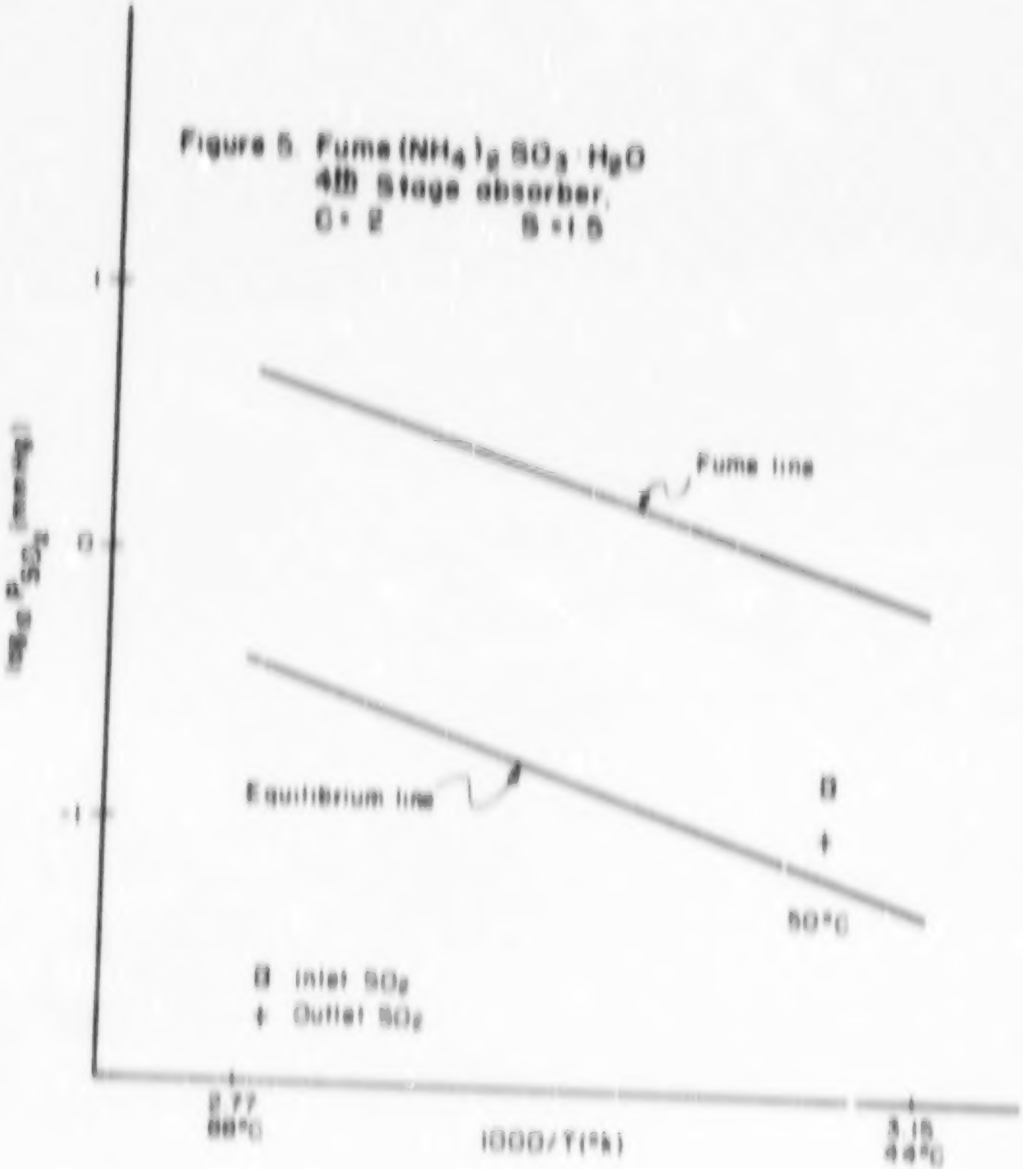

Figure 5 Fume $(NH_4)_2SO_3$ $H_2O$
4th Stage absorber,
C = 2 S = 1.5

# APPENDIX F

## CONDENSED OPERATING DATA

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## TABLE F-1. ABSORBER OPERATING DATA, ABS-1 TEST SERIES

| Test No. | A-2 | A-3 | A-3A | A-4 | A-4A | A-1B | A-1B |
|---|---|---|---|---|---|---|---|
| Flow rates | | | | | | | |
| Liquor, gal/min | | | | | | | |
| To D-1 | 26.5 | 26.5 | 25.0 | 25.0 | 27.0 | 26.0 | 26.0 |
| To D-2 | 15.0 | 15.0 | 15.0 | 15.0 | 16.0 | 16.0 | 16.0 |
| To D-3 | 15.0 | 16.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 |
| Makeup water to F-1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.3 | 0.2 | 0.2 |
| Gas, cfm (@ 125°F) | 1,100 | 1,100 | 1,000 | 1,100 | 1,100 | 1,100 | 1,100 |
| Liquor concentrations | | | | | | | |
| D-1 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 16.0 | 12.1 | 12.0 | 8.5 | 7.6 | 10.9 | 13.7 |
| $S/C_A$ | 0.81 | 0.82 | 0.80 | 0.84 | 0.83 | 0.76 | 0.74 |
| Out | | | | | | | |
| $C_A$ | 15.1 | 12.6 | 11.8 | 8.5 | 7.3 | 10.8 | 13.7 |
| $S/C_A$ | 0.81 | 0.82 | 0.81 | 0.85 | 0.84 | 0.79 | 0.75 |
| D-2 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 15.6 | 13.1 | 13.6 | 10.3 | 7.8 | 7.6 | 8.9 |
| $S/C_A$ | 0.61 | 0.74 | 0.67 | 0.66 | 0.79 | 0.73 | 0.74 |
| Out | | | | | | | |
| $C_A$ | 16.1 | 13.3 | 13.6 | 10.5 | 7.9 | 7.7 | 9.1 |
| $S/C_A$ | 0.62 | 0.75 | 0.68 | 0.68 | 0.71 | 0.75 | 0.74 |
| D-3 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 8.0 | 7.8 | 7.0 | 5.3 | 4.8 | 6.0 | 5.0 |
| $S/C_A$ | 0.68 | 0.76 | 0.75 | 0.74 | 0.77 | 0.86 | 0.83 |
| Out | | | | | | | |
| $C_A$ | 8.1 | 8.2 | 7.3 | 5.5 | 5.1 | 6.3 | 5.6 |
| $S/C_A$ | 0.68 | 0.75 | 0.76 | 0.73 | 0.76 | 0.84 | 0.81 |
| $SO_2$ concentrations, ppm | | | | | | | |
| To D-1 | 2,160 | 2,240 | 2,320 | 2,160 | 2,630 | 2,560 | 2,400 |
| To D-2 | 1,720 | 520 | 1,680 | 1,200 | 1,600 | 960 | 960 |
| To D-3 | 200 | 260 | 240 | 160 | 240 | 630 | 600 |
| Stack | 120 | 160 | 240 | 200 | 240 | 360 | 280 |
| Overall $SO_2$ removal, % | 94.4 | 91.7 | 89.7 | 90.7 | 90.2 | 85.9 | 88.3 |
| Temperature, °F | | | | | | | |
| Liquors | | | | | | | |
| Prewash sump | 118 | 121 | 121 | 112 | 127 | 120 | 125 |
| D-1 out | 126 | 127 | 128 | 129 | 128 | 126 | 135 |
| D-2 out | 127 | 126 | 130 | 129 | 125 | 125 | 130 |
| D-3 out | 123 | 125 | 126 | 126 | 124 | 121 | 126 |
| Gas | | | | | | | |
| To prewash | 265 | 278 | 280 | 284 | 280 | 285 | 290 |
| To D-1 | 120 | 121 | 121 | 122 | 125 | 120 | 123 |
| To D-2 | 126 | 128 | 129 | 130 | 126 | 128 | 135 |
| To D-3 | 127 | 127 | 129 | 128 | 126 | 125 | 130 |
| To stack | 126 | 124 | 126 | 125 | 124 | 122 | 126 |
| Ambient | 71 | 55 | 69 | 56 | 57 | 50 | 63 |
| Relative humidity, % | 61 | 58 | 81 | 55 | 64 | 51 | 37 |
| Predicted minimum temperature at which steam plume forms, °F | 165 | 175 | 155 | 157 | 190 | 163 | 155 |
| Reheat temperature, °F | 152 | 185 | 170 | 175 | 216 | 185 | None |
| Percent opacity [a,b] | 15/60 | 5-10/60 | 5/30 | 15 | 5/30 | 5/20 | 60/80 |

a. Plume opacity read at one stack diameter distance above the stack.
b. Plume opacity read at approximately 30 ft from stack tip.

## TABLE F-2. FUME CONTROL STUDIES DATA, AP TEST SERIES

| Test No. | AP-A1 | AP-D1 | AP-A2 | AP-D2 | AP-B1 | [illegible] | [illegible] |
|---|---|---|---|---|---|---|---|
| Liquor concentrations | | | | | | | |
| D-1 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 11.70 | 11.25 | 11.20 | 12.12 | 11.51 | 8.91 | 9.11 |
| $S/C_A$ | 0.80 | 0.82 | 0.81 | 0.81 | 0.83 | 0.78 | 0.82 |
| Out | | | | | | | |
| $C_A$ | 11.53 | 11.31 | 12.09 | 12.11 | 11.70 | 8.15 | 9.06 |
| $S/C_A$ | 0.91 | 0.86 | 0.85 | 0.85 | 0.83 | 0.82 | 0.83 |
| D-2 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 9.08 | 11.71 | 9.08 | 7.06 | 8.61 | 6.81 | 7.81 |
| $S/C_A$ | 0.83 | 0.77 | 0.69 | 0.74 | 0.71 | 0.75 | 0.73 |
| Out | | | | | | | |
| $C_A$ | 9.56 | 11.61 | 8.81 | 7.16 | 8.66 | 6.71 | 7.50 |
| $S/C_A$ | 0.83 | 0.77 | 0.71 | 0.75 | 0.73 | 0.77 | 0.72 |
| D-3 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 2.72 | 3.60 | 2.61 | 1.99 | 2.28 | 1.13 | 1.78 |
| $S/C_A$ | 1.03 | 0.85 | 0.86 | 0.47 | 0.67 | 1.00 | 0.93 |
| Out | | | | | | | |
| $C_A$ | 2.37 | 3.70 | 2.83 | 1.99 | 2.42 | 1.07 | 1.78 |
| $S/C_A$ | 1.06 | 0.95 | 0.96 | 1.13 | 0.96 | 1.01 | 0.93 |
| D-4 | | | | | | | |
| In | | | | | | | |
| $C_A$ | 0.50 | 1.12 | 0.81 | 0.11 | 0.38 | 0.03 | 1.28 |
| $S/C_A$ | 1.94 | 1.18 | 0.91 | 1.11 | 1.44 | 3.00 | 0.90 |
| Out | | | | | | | |
| $C_A$ | 0.61 | 1.12 | 1.11 | 0.20 | 0.46 | 0.08 | 0.18 |
| $S/C_A$ | 1.84 | 1.18 | 0.83 | 2.02 | 1.37 | 1.91 | 0.91 |
| Gas temperatures, °F | | | | | | | |
| To prewash | 202 | 210 | 220 | 230 | 225 | 220 | 212 |
| To D-1 | 118 | 122 | 121 | 121 | 128 | 118 | 115 |
| To D-2 | 118 | 119 | 120 | 127 | 127 | 117 | 117 |
| To D-3 | 116 | 117 | 118 | 121 | 126 | 115 | 112 |
| To D-4 | 111 | 111 | 121 | 120 | 121 | 113 | 115 |
| Stack | 175 | 168 | 161 | 181 | 174 | 167 | 161 |
| Liquor temperatures, °F | | | | | | | |
| D-1 out | 116 | 121 | 121 | 126 | 128 | 116 | 111 |
| D-2 out | 112 | 116 | 120 | 121 | 125 | 115 | 110 |
| D-3 out | 110 | 113 | 115 | 121 | 126 | 113 | 110 |
| D-4 out | 110 | 112 | 115 | 121 | 122 | 113 | 110 |
| $SO_2$ concentrations, ppm | | | | | | | |
| To D-1 | 1,820 | 1,700 | 2,760 | 2,720 | 2,640 | [illegible] | 1,780 |
| From D-1 | 1,500 | 1,580 | 2,500 | 2,380 | 2,420 | 1,820 | 2,220 |
| To fume on D-1 | a | 1,615 | 1,917 | [illegible] | [illegible] | 1,757 | 1,883 |
| To D-2 | 1,500 | 1,580 | 2,500 | 2,380 | 2,420 | 1,820 | 2,220 |
| From D-2 | 1,120 | 900 | 1,120 | 1,600 | 1,600 | 1,050 | 970 |
| To fume on D-2 | a | 2,805 | 1,219 | [illegible] | 2,178 | [illegible] | [illegible] |
| To D-3 | 1,120 | 900 | 1,120 | 1,600 | 1,600 | 1,050 | 970 |
| From D-3 | 1,080 | 840 | 1,010 | 1,360 | 1,360 | 1,000 | 950 |
| To fume on D-3 | [illegible] | a | a | a | a | [illegible] | a |
| To D-4 | 1,080 | 840 | 1,010 | 1,360 | 1,360 | 1,000 | 950 |
| From D-4 | 1,040 | 780 | 910 | 1,280 | 1,220 | 910 | 890 |
| To fume on D-4 | [illegible] | [illegible] | a | [illegible] | [illegible] | [illegible] | a |
| Overall $SO_2$ removal, % | 43 | 55 | 63 | [illegible] | 54 | [illegible] | [illegible] |
| Plume opacity, % at the [illegible] of [illegible], °F | | | | | | | |
| 135 | 10 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 145 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 155 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 165 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 175 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 185 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 195 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 205 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 215 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| 225 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

a. Statistical calculations show that it is impossible to [illegible] these concentrations.

TABLE 5-3. FINE CONTROL STUDIES DATA, UNMODIFIED ABSORBER - [illegible] SERIES

[illegible]

## [illegible]

[illegible]

TABLE F-5. ACIDULATOR-STRIPPER OPERATING DATA, ABS-I TEST SERIES

| Test No. | AS-4 | AS-5 | AS-6 | AS-7 | AS-8 | AS-9 |
|---|---|---|---|---|---|---|
| Product liquor to acidulator-stripper | | | | | | |
| Chemical analysis, S, g/l | | | | | | |
| $NH_4HSO_3$ | 84.71 | 84.32 | 84.32 | 84.32 | 84.32 | 84.71 |
| $(NH_4)_2SO_3$ | 26.10 | 25.73 | 23.85 | 26.45 | 23.81 | 26.61 |
| $(NH_4)_2SO_4$ | 22.74 | 21.12 | 22.81 | 22.79 | 23.43 | 20.26 |
| pH | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 |
| Specific gravity, g/ml | 1.195 | 1.194 | 1.193 | 1.192 | 1.192 | 1.192 |
| Flow rate, gal/min | 1.6 | 1.6 | 1.7 | 1.6 | 1.6 | 1.5 |
| Sulfuric acid to acidulator | | | | | | |
| Chemical analysis, % $H_2SO_4$ | 93.7 | 93.7 | 93.7 | 93.7 | 93.7 | 93.7 |
| Flowrate, gal/min | 0.28 | 0.28 | 0.28 | 0.34 | 0.34 | 0.34 |
| Stoichiometry[a] | 1.42 | 1.38 | 1.34 | 1.76 | 1.81 | 1.85 |
| Stripping gas (air) flowrate, cfm | 5 | 10 | 15 | 5 | 10 | 15 |
| Overall $SO_2$ recovery efficiency, % | 86 | 88 | 91 | 95 | 97 | 96 |
| Temperature, °F | | | | | | |
| Product liquor feed | 137 | 136 | 134 | 138 | 139 | 140 |
| Acidulator liquor outlet | 124 | 124 | 123 | 125 | 128 | 128 |
| Stripper liquor outlet | 111 | 109 | 106 | 112 | 115 | 113 |
| Stripping gas inlet | 58 | 56 | 55 | 56 | 54 | 56 |

a: The mol ratio of $H^+$ to $NH_4^+$ where the $NH_4^+$ is supplied by the ammonium sulfite and bisulfite.

## TABLE F-6. ACIDULATION AND STRIPPING DATA

| Test No. | AS-1 | AS-2 | AS-3 | AS-3A |
|---|---|---|---|---|
| Test conditions | | | | |
| Feed liquor, gal | 30 | 30 | 30 | - |
| Pounds of sulfuric acid | 73.5 | 72.0 | 78.0 | - |
| Acid feed rate, gal/min | 0.31 | 0.31 | 0.31 | - |
| Stripping gas rate, cfm | 5 | 10 | 15 | 15 |
| Temperatures, °F | | | | |
| Acidulator feed | 88 | 81.5 | 85.0 | - |
| Acidulator gas outlet | 84 | 78.3 | 80.7 | - |
| Sulfuric acid feed | 87 | 74.3 | 77.5 | - |
| Stripper feed | 138 | 113.7 | 139.0 | 160 |
| Air to stripper | 90 | 75.7 | 81.7 | 82 |
| Stripper effluent | 109 | 85.0 | 88.0 | 87 |
| Stripper outlet gas | 135 | 107.6 | 123.3 | 128.5 |
| Liquor | | | | |
| Absorber product to acidulator | | | | |
| Sulfite sulfur, g/l | 33.6 | 32.49 | 30.64 | - |
| Bisulfite sulfur, g/l | 102.3 | 103.18 | 101.49 | - |
| Sulfate sulfur, g/l | 27.2 | 33.90 | 33.64 | - |
| Total sulfur, g/l | 163.2 | 169.56 | 165.76 | - |
| Specific gravity, g/ml | 1.236 | 12.40 | 1.242 | - |
| pH | 5.8 | 5.8 | 5.7 | - |
| Sulfuric acid, % $H_2SO_4$ | 91.0 | 88.9 | 91.8 | - |
| Acidulator effluent | | | | |
| Sulfite sulfur, g/l | 0.0 | 0.0 | 0.0 | - |
| Bisulfite sulfur, g/l | 9.1 | 6.25 | 0.0 | - |
| Sulfate sulfur, g/l | 99.1 | 105.07 | 105.86 | - |
| Total sulfur, g/l | 131.9 | 162.93 | 162.64 | - |
| Free $SO_2$,[a] g/l | 47.6 | 61.60 | 62.30 | - |
| Bisulfate sulfur, g/l | 0.0 | 0.0 | 5.64 | - |
| Specific gravity, g/ml | 1.230 | 1.239 | 1.241 | - |
| pH | 2.0 | 1.8 | 1.56 | - |
| Stripper effluent | | | | |
| Sulfite sulfur, g/l | 0.0 | 0.0 | 0.0 | 0.0 |
| Bisulfite sulfur, g/l | 1.9 | 6.54 | 0.0 | 0.0 |
| Sulfate sulfur, g/l | 100.9 | 111.96 | 106.47 | 115.50 |
| Total sulfur, g/l | 108.6 | 120.44 | 115.72 | 123.90 |
| Free $SO_2$,[a] g/l | 11.6 | 3.88 | 0.68 | 0.12 |
| Bisulfate sulfur, g/l | 0.0 | 0.0 | 8.92 | 8.33 |
| Specific gravity, g/ml | 1.208 | 1.223 | 1.231 | 1.237 |
| pH | 4.6 | 4.76 | 2.13 | 2.20 |
| Acidulation-stripping efficiency | | | | |
| Actual stoichiometry[b] | 0.98 | 0.994 | 1.148 | - |
| Percent of $SO_2$ to acidulator that is evolved in acidulator | 93.3 | 95.4 | 100 | - |
| Percent of $SO_2$ to stripper that is removed in the stripper | 81.1 | 93.6 | 98.9 | 82.4 |
| Percent of $SO_2$ removed overall | 95.7 | 97.3 | 99.7 | 82.4 |

a. Free $SO_2$ is that $SO_2$ that has been released by acidulation but is still in solution.

b. This stoichiometry refers to the mol ratio of the $H^+$ ion to the $NH_4^+$ ion where the $NH^+$ ion is supplied by the ammonium sulfite and bisulfite.

## TABLE F-7. ACIDULATION AND STRIPPING DATA

| Test No. | AS-4 | AS-6 | AS-8 | AS-9 | AS-10 | AS-11 | AS-12 |
|---|---|---|---|---|---|---|---|
| Flow rates | | | | | | | |
| Feed liquor, gpm | 0.5 | 0.5 | 0.45 | 0.45 | 0.45 | 0.65 | 0.65 |
| Sulfuric acid, gpm | 0.08 | 0.078 | 0.076 | 0.076 | 0.076 | 0.076 | 0.076 |
| Stripping gas (air), cfm | 10 | 5 | 5 | 5 | 5 | 10 | 15 |
| Temperatures, °F | | | | | | | |
| Water bath | - | - | 140 | - | - | - | - |
| Feed liquor | 115 | 116.8 | 117.5 | 141 | 68.5 | 70 | 114 |
| Sulfuric acid | 74 | 86.7 | 61.7 | 59.7 | 68.5 | 69.7 | 68 |
| Stripping gas | 71 | 83.8 | 59.7 | 57.7 | 65.5 | 63.0 | 78 |
| Stripper effluent | 82.3 | 98.5 | 85.5 | 93.3 | 75.0 | 70.7 | 86 |
| Stripper exit gas | 120.3 | 110.0 | 99.3 | 110.0 | 75.0 | 80.0 | 105 |
| Liquor analyses | | | | | | | |
| Absorber product to acidulator | | | | | | | |
| Sulfite sulfur, g/l | 24.25 | 32.22 | 34.92 | 31.71 | 25.33 | 26.31 | 25.27 |
| Bisulfite sulfur, g/l | 95.63 | 104.19 | 105.49 | 105.80 | 102.29 | 104.05 | 97.26 |
| Sulfate sulfur, g/l | 42.21 | 29.69 | 17.22 | 28.39 | 27.93 | 27.11 | 28.43 |
| Specific gravity, g/ml | 1.260 | 1.234 | 1.262 | 1.237 | 1.221 | 1.223 | 1.216 |
| pH | 5.7 | 5.8 | 5.8 | 5.57 | 5.65 | 5.6 | 5.9 |
| Sulfuric acid, % $H_2SO_4$ | 90.1 | 90 | 91.4 | 91.7 | 91.9 | 92.2 | 92.8 |
| Stripper effluent | | | | | | | |
| Sulfite sulfur, g/l | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Bisulfite sulfur, g/l | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Sulfate sulfur, g/l | 94.69 | 108.01 | 102.34 | 97.92 | 75.16 | 79.76 | 82.73 |
| Bisulfate sulfur, g/l | 34.31 | 9.12 | 18.92 | 21.10 | 42.13 | 40.49 | 29.91 |
| Free $SO_2$, g/l | 2.16 | 0.44 | 0.40 | 0.60 | 2.69 | 0.99 | 0.54 |
| Total sulfur, g/l | 130.08 | 117.35 | 121.47 | 120.22 | 118.64 | 120.74 | 112.90 |
| Specific gravity, g/ml | 1.234 | 1.220 | 1.231 | 1.227 | 1.218 | 1.223 | 1.208 |
| pH | 1.8 | 2.3 | 2.0 | 1.6 | 1.1 | 0.97 | 1.5 |
| Acidulation-stripping efficiency | | | | | | | |
| Actual stoichiometry[a] | 1.163 | 1.051 | 1.107 | 1.101 | 1.225 | 1.258 | 1.202 |
| Percent acidulation | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Percent of released $SO_2$ that is stripped | 99.1 | 99.8 | 99.2 | 99.8 | 98.9 | 99.6 | 99.8 |
| Tower packing height, ft | 30 | 30 | 30 | 30 | 20.3 | 20.3 | 20.3 |

[a] Stoichiometry refers to the mol ratio of the $H^+$ ion to the $NH_4^+$ ion where the $NH^+$ ion is supplied by ammonium sulfite and bisulfite.

# APPENDIX G

# DESIGN OF A PILOT PLANT AMMONIUM SULFATE DECOMPOSER

## CONTENTS

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## FOREWORD

In 1974 EPA contracted with Dr. Richard M. Felder (Associate Professor of Chemical Engineering at North Carolina State University) to conduct an in-depth design study for an electrical thermal decomposer that would decompose ammonium sulfate to ammonium bisulfate and ammonia. The study (done in two parts) was performed under EPA purchase order No. 4-02-04510. Dr. Felder based his study on rate and equilibrium data taken from earlier tests conducted by Chemico and TVA and from a literature survey.

The first report (May 30, 1974) covered the reaction kinetics and reactor sizing based on a first-order reversible reaction. An addendum to the first report (June 12, 1974) covered the possibility of an irreversible reaction and its effect on holdup volume. Data showed that no significant discrepancies between a reversible and irreversible reaction occurred until the melt temperature reached 750°F. A melt temperature of 700°F was specified to eliminate the problem. The third report (June 20, 1974) dealt with power input, electrode spacing, and electrode immersion depth.

# DESIGN OF A PILOT PLANT AMMONIUM SULFATE DECOMPOSER*

## I. Reaction Kinetics and Reactor Sizing

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May 30, 1978

*Work performed under EPA Purchase Order #4-02-04510

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## ABSTRACT

Rate and equilibrium data for the decomposition of ammonium sulfate have been analyzed and used to determine a rate law. This law has in turn been used to derive equations for the approximate sizing of a continuous salt-bath furnace in which to carry out the decomposition reaction.

## INTRODUCTION

During the last decade, interest in reducing air pollution in America and abroad has increased at an accelerated rate. One particularly objectionable pollutant is sulfur dioxide released to the atmosphere in huge quantities by public utilities and other consumers of fossil fuels. Several processes to remove sulfur oxides from stack gases are being tested currently in commercial power plants, and in addition a number of "second generation" processes are being evaluated in pilot plants. Ammonia scrubbing--bisulfate regeneration is a promising "second generation" process being tested jointly by the Environmental Protection Agency and the Tennessee Valley Authority. The ammonia scrubbing--bisulfate regeneration process consists of a set of integrated unit operations, all of which have been proven individually. The pilot plant program is directed toward optimizing conditions for an integrated process so that $SO_2$ can be recovered efficiently and economically in an operation having a high service factor.

One unit operation in the processing sequence is the decomposition of ammonium sulfate to yield ammonia and ammonium bisulfate. This operation was tested on a large scale in a government-financed Plancor plant during World War II. Although a large decomposer was designed and operated, design details were withheld from reports on the operation, and Chemical Construction Company--the developer of the process--has not been able to locate the design and supporting calculations. In the absence of these calculations a decomposer must be designed from the meager data contained in correspondence between Chemico and the sponsoring government agency and Chemico's reports to that agency.

This report deals with one phase of the decomposer design--the correlation of available kinetic and equilibrium data for the decomposition reaction and the sizing of the pilot plant reactor using this correlation.

The first section of the report presents equations which can be used to estimate the reaction volume needed to achieve a desired conversion at a specified reaction temperature. Subsequent sections briefly summarize the kinetic and equilibrium data and the analysis which led to the proposed design equations. For the sake of brevity detailed derivations of the equations have not been included in the report, but they can be furnished upon request.

## SUMMARY OF REACTOR DESIGN EQUATIONS

Rate and equilibrium data for the reaction

$$(NH_4)_2SO_4 \rightleftharpoons NH_4HSO_4 + NH_3 \qquad (1)$$

have been analysed and used to determine a rate law. The following equations based on this rate law are proposed for the sizing of a continuous salt-bath furnace in which to carry out this reaction.

Let

$T$ = reactor temperature, °K

$\gamma$ = ratio of steam feed rate to ammonium sulfate feed rate, lb $H_2O$/lb $(NH_4)_2SO_4$

$z$ = mass fraction of bisulfate in the melt

Calculate

$$k\ (hr^{-1}) = 6.22 \times 10^7 \exp[-11{,}320/T] \qquad (2)$$

$$x = \frac{z/115}{(z/115) + (1 - z)/132} \qquad (3)$$

$$\bar{x} = [0.185(7.333\,\gamma - 1)^2 + 6.307\,\gamma]^{1/2} - 0.43(7.333\,\gamma - 1) \qquad (4)$$

$$\tau\ (hr) = \frac{0.99\ x\ (1 - 0.1288\ x)}{k(\bar{x} - x)} \qquad (5)$$

where $k$ is a first-order decomposition rate constant, $x$ is the mol fraction of bisulfate in the melt, $\bar{x}$ is the equilibrium value of $x$ at the given reaction conditions, and $\tau$, the reactor space time, is

$$\tau = \frac{110.4\ V(ft^3)}{q_s(lb/hr)} \qquad (6)$$

In Eq. (6), V is the melt volume and $q_s$ is the feed rate of ammonium sulfate. Once $\tau$ has been calculated from Eqs. (2)-(5), the melt volume V may be determined for a given feed rate $q_s$ or vice versa from Eq. (6).

Once V is known, the mass of the reactor contents may be estimated approximately as

$$M\ (lb) = 132\ V(ft^3) \qquad (7)$$

The value of H calculated using Eq. (7) takes into account the quantity of melt expected to penetrate into the refractory lining of the salt bath.*

For example, suppose the reaction is to be run at 700°F (644.4°K), with $\gamma$ = 0.2 (lb $H_2O$/lb$(NH_4)_2SO_4$), and a bisulfate mass fraction z = 0.85 is desired with a feed rate of 3.4 lb$(NH_4)_2SO_4$/min. Then from Eqs. (2)-(5)

$$k = 1.46 \text{ hr}^{-1}$$

$$x = 0.867 \text{ mols } NH_4HSO_4/\text{mol}$$

$$\bar{\bar{x}} = 0.94 \text{ mols } NH_4HSO_4/\text{mol}$$

$$\tau = 7.15 \text{ hr}$$

and from Eq. (6)

$$V = \frac{(7.15)(60 \times 3.4)}{110.4} = 13.2 \text{ ft}^3$$

which corresponds to an approximate holdup of

$$(13.2 \times 132) = 1742 \text{ lb.}$$

The influence of the reaction temperature and the steam to sulfate feed ratio on the required melt volume are illustrated by the following results:

| T(°F) | $\gamma$(lb $H_2O$/lb$(NH_4)_2SO_4$) | V(ft³) |
|---|---|---|
| 700 | 0.2 | 13.2 |
| 725 | 0.2 | 9.1 |
| 750 | 0.2 | 6.8 |
| 700 | 0.1 | 19.3 |
| 700 | 0.2 | 13.2 |
| 700 | 0.3 | 11.2 |

The data used to derive Eqs. (2)-(5) are highly scattered, and it is recommended that an overdesign factor of approximately two be applied when designing a plant unit using these equations.

---

*An Ajax Electric Company Report (1971) noted that in an experiment in which 420 lb of sulfate were charged, 70 lb penetrated into the reactor walls. As an approximation, the same ratio of melt penetrating to total melt has been assumed in deriving Eq. (7).

## REACTION KINETICS AND EQUILIBRIUM

For the reaction

$$(NH_4)_2SO_4 \rightleftharpoons NH_4HSO_4 + NH_3 \qquad (7)$$

a rate law of the following form is proposed:

$$r = k(C - \tilde{C}) \qquad (8)$$

where

r = homogeneous decomposition rate of ammonium sulfate, lb-mols/ft$^3$·hr

k = first-order rate constant, hr$^{-1}$

C = concentration of ammonium sulfate in the melt, lb-mols/ft$^3$

$\tilde{C}$ = equilibrium concentration of ammonium sulfate at the prevailing reaction conditions, lb-mols/ft$^3$

Based on this rate law, the following equation relates the conversion in a continuous molten salt bath reactor to the melt volume and ammonium sulfate feed rate:

$$\frac{x(1 - 0.1288\ x)}{\tilde{x} - x} = k\ \frac{110.8}{1 - Y_s}\ \frac{V}{q_s} \qquad (9)$$

where

x = mol fraction of bisulfate in the melt

$\tilde{x}$ = equilibrium value of x

$Y_s$ = fraction of the sulfate feed that sublimates before melting

V = melt volume, ft$^3$

$q_s$ = feed rate of ammonium sulfate, lb/hr

The equilibrium conversion $\tilde{x}$ is determined as follows. If $\tilde{x}_o$ is the equilibrium conversion at the melt temperature in the absence of a stripping gas (such as steam) bubbling through the melt, and

$$\alpha = \frac{\tilde{x}_o\ (T)}{1 - \tilde{x}_o\ (T)} \qquad (10)$$

and if $\phi$ is the mol ratio of stripping gas to ammonium sulfate feed, then

$$\hat{x} = \frac{-a(\phi-1)+[a^2(\phi-1)^2+4(a+1)a\phi]^{1/2}}{2(a+1)} \qquad (11)$$

If the stripping gas is steam, then the mol ratio $\phi$ equals 7.333$\gamma$, where $\gamma$ is the mass ratio of steam fed to ammonium sulfate fed.

To design a reactor to operate at a temperature T with a given stripping gas ratio $\phi$, it is necessary to specify the values of the equilibrium conversion $x_e(T)$, the rate constant $k(T)$, and the fractional sublimation $y_s(T)$. $\hat{x}$ is calculated from $x_e$ and $\phi$ using Eqs. (10) and (11), and the values of $\hat{x}$, k and $y_s$ are then substituted into Eq. (9). The three remaining variables in this equation are the mol fraction of bisulfate in the melt (x), the melt volume (V) and the sulfate feed rate ($q_s$); any two of these variables may be specified, and the third variable may then be calculated from Eq. (9).

In terms of the variables defined above, the reactor "space time," or ratio of the melt volume to the volumetric flow rate of the sulfate feed, is

$$\tau(\mathrm{hr}) = \frac{110.8V(\mathrm{ft}^3)}{q_s(\mathrm{lb/hr})} \qquad (12)$$

where the numerator is the total mass of the melt. The mean residence time in the reactor--a less useful quantity than the space time from the standpoint of design--is approximately [illegible]% of $\tau$ when x is 0.85.

The principal design equation--Eq. (9)--is derived assuming that the salt bath behaves like a perfect mixer, and that the reaction occurs with sufficient steam present to suppress the decomposition of ammonium bisulfate to ammonium pyrosulfate and water. Eq. (11) for the equilibrium conversion is derived assuming that the reaction of Eq. (7) is governed by the equilibrium relationship

$$K = \frac{\hat{x}p_{NH_3}}{(1-\hat{x})} \qquad (13)$$

and that the partial pressure of ammonia equals the total pressure (a constant) times the ratio (mols $NH_3$)/(mols $NH_3$ + mols stripping gas).

The sections that follow summarize the available data which may be used to infer the values of $y_s$, $x_e$ and k(T).

(a) Reaction Equilibrium

The fact that the ammonium sulfate decomposition reaction must be treated as reversible is made clear in several referenced studies. Kiyoura and Urano (1970) show a dependence of the equilibrium partial pressure of ammonia on temperature; a Shell Development report (1971), invalidates the quantitative results obtained by Kiyoura and Urano but corroborates the reversibility of the reaction.

The only useful information regarding the equilibrium point of the decomposition reaction is some relatively sketchy data given in an internal TVA report (1968). In this study, batch decompositions were carried out at temperatures between 600°F and 800°F, and it was found that the equilibrium conversion of sulfate to bisulfate fell in the range 0.83-0.86 for temperatures of 700°F and higher (runs at 600°F and 650°F were terminated before equilibrium was achieved). In these runs a gas ($N_2$ in all but one run) was swept over but was not bubbled through the melt, and consequently a value of x in the range 0.83 - 0.86 may be taken as an approximation for the variable $x_e$ of Eq. (10). In deriving Eq. (4), a value of 0.86 was assumed.

An assumed equilibrium conversion based on this data must not be taken as anything but a rough estimate, however, for the following reasons:

(1) The true equilibrium conversion depends on the partial pressure of ammonia, which is not known in the TVA experiments.

(2) The values 0.83 - 0.86 were obtained by absorbing the emitted $NH_3$ in a scrubbing solution and titrating with sulfuric acid. Subsequent chemical analyses of the final melt showed conversions above 90%, a discrepancy which was never explained.

(3) No steam was present in the stripping gas, so that the bisulfate undoubtedly decomposed to ammonium pyrosulfate. The effect of this phenomenon would be expected to be an enhanced equilibrium conversion.

(b) Reaction Rate

Data contained in a pair of Chemical Construction Company reports (1963) and the TVA report (1968) have been used to estimate values of the first-order rate constant k of Eq. (9).

The 1963 reports present data for two reactors: a three-phase reactor with a holdup of approximately 5500 lbs, and a smaller single-phase reactor with a holdup of approximately 1600 lbs which was built specifically to study the effects of steam on the reactor performance. Values for the following quantities are specified or are directly calculable from data contained in the report:

$T$ (melt temperature)
$V$ (melt volume)
$q_s$ (sulfate feed rate)
$x$ (mol fraction of bisulfate in the melt)

In addition, the data for the small single-phase reactor include values of

$y$ (lb steam/lb sulfate feed)
$T_s$ (steam temperature)

The data contained in the Chemico reports have been analysed as follows. For each run values of $y_s$ and $x_s$ were assumed, $x$ was calculated from Eq. (10), $\bar{x}$ was calculated from Eq. (11), $k$ was determined from Eq. (9), and the corresponding value of the space time $\tau$ was calculated from Eq. (12). The results are summarized in Table 1.

Conversion vs. time ($x$ vs. $t$) data are also presented in Figure 2 of the TVA report (1968). If the rate law of Eq. (2) is obeyed a plot of log $(1 - x/\bar{x})$ vs. $t$ should yield a straight line with slope $-k$. Such plots are shown in Figure 1; the time $t=0$ on this graph corresponds to 25 minutes after the start of each run, by which time the melt had supposedly reached the specified reaction temperature. The near linearity of the isotherms appears to validate the assumed rate law. The lines have been drawn in by visual inspection.

In Figure 2 all of the calculated rate constants are shown on an Arrhenius plot of log $k$ vs. $1/T$. Also shown is a single value calculated for a Salem, Oregon pilot plant reactor from data given in the Fiancor 1865 report (1946).

The significant point that emerges from an inspection of Figure 2 is that the rate constants calculated for each given temperature are scattered, but all have the same magnitude. Considering the differences between the systems for which these constants were determined, the imprecision of the equilibrium data, the assumptions required to obtain the rate constants and the complicating phenomena which could not be taken into account (e.g. the decomposition of the bisulfate and the discrepancies between results obtained using different analytical methods in the TVA batch runs and the low inlet steam temperatures in many of the Chemico runs), this result is extremely encouraging.

A line has been drawn somewhat arbitrarily on Figure 2 to determine the temperature dependence of the rate constant. The fit was made to the Chemico results, which more nearly correspond

## TABLE 1. CHEMICO (1943) RATE DATA

| T(°F) | Assumed<br>$y_s$ | <br>$\bar{n}_n$ | Y<br>(lb steam / lb sulfate) | $T_s$(°F) | t (hr) | x<br>(mole $NH_4HSO_4$ / mol total) | k(hr$^{-1}$) |
|---|---|---|---|---|---|---|---|
| ***720 | 0.03 | 0.86 | 0 | - | 3.01 | 0.750 | 2.69 |
| ***765 | 0.03 | 0.8[illegible] | 0 | - | 2.87 | 0.766 | 3.23 |
| ***760 | 0.03 | 0.86 | 0 | - | 2.60 | 0.755 | 3.10 |
| ***760 | 0.03 | 0.86 | 0 | - | 3.48 | 0.759 | 2.46 |
| ***760 | 0.03 | 0.86 | 0 | - | 2.86 | 0.760 | 3.01 |
| ***765 | 0.03 | 0.86 | 0 | - | 2.76 | 0.753 | 2.85 |
| *760 | 0.01 | 0.86 | 0.15 | 600 | 7.1[illegible] | 0.896 | 1.79 |
| *760 | 0.01 | 0.86 | 0.31 | 655 | 6.86 | 0.909 | 2.59 |
| *760 | 0.01 | 0.86 | 0.31 | 645 | 6.74 | 0.905 | 2.40 |
| *760 | 0.01 | 0.86 | 0.31 | 710 | 6.74 | 0.922 | 3.71 |
| *675 | 0.01 | 0.86 | 0.19 | 660 | 3.74 | 0.783 | 1.21 |
| *660 | " | " | 0.16 | 655 | 3.88 | 0.726 | 0.821 |
| *660 | " | " | 0.17 | 610 | 3.74 | 0.732 | 0.873 |
| *690 | " | " | 0.21 | 650 | 4.63 | 0.809 | 1.18 |
| *690 | " | " | 0.21 | 650 | 4.63 | 0.812 | 1.21 |
| *690 | " | " | 0.29 | 670 | 6.60 | 0.81[illegible] | 0.956 |
| *685 | " | " | 0.30 | 670 | 6.60 | 0.824 | 0.864 |
| *685 | " | " | 0.30 | 660 | 6.60 | 0.817 | 0.818 |
| *705 | " | " | 0.18 | 655 | 4.86 | 0.83[illegible] | 1.56 |
| *705 | " | " | 0.20 | 650 | 4.96 | 0.836 | 1.46 |
| *705 | " | " | 0.16 | 620 | 4.96 | 0.827 | 1.41 |
| *705 | " | " | 0.22 | 700 | 4.96 | 0.829 | 1.32 |
| *705 | " | " | 0.00 | - | 4.96 | 0.771 | 1.58 |
| *705 | " | " | 0.00 | - | 4.96 | 0.759 | 1.37 |
| *705 | " | " | 0.10 | 580 | 4.72 | 0.786 | 1.16 |
| *700 | " | " | 0.10 | 610 | 4.72 | 0.781 | 1.09 |
| *700 | " | " | 0.10 | 620 | 4.72 | 0.787 | 1.15 |

*** 3-phase reactor
  * 1-phase reactor

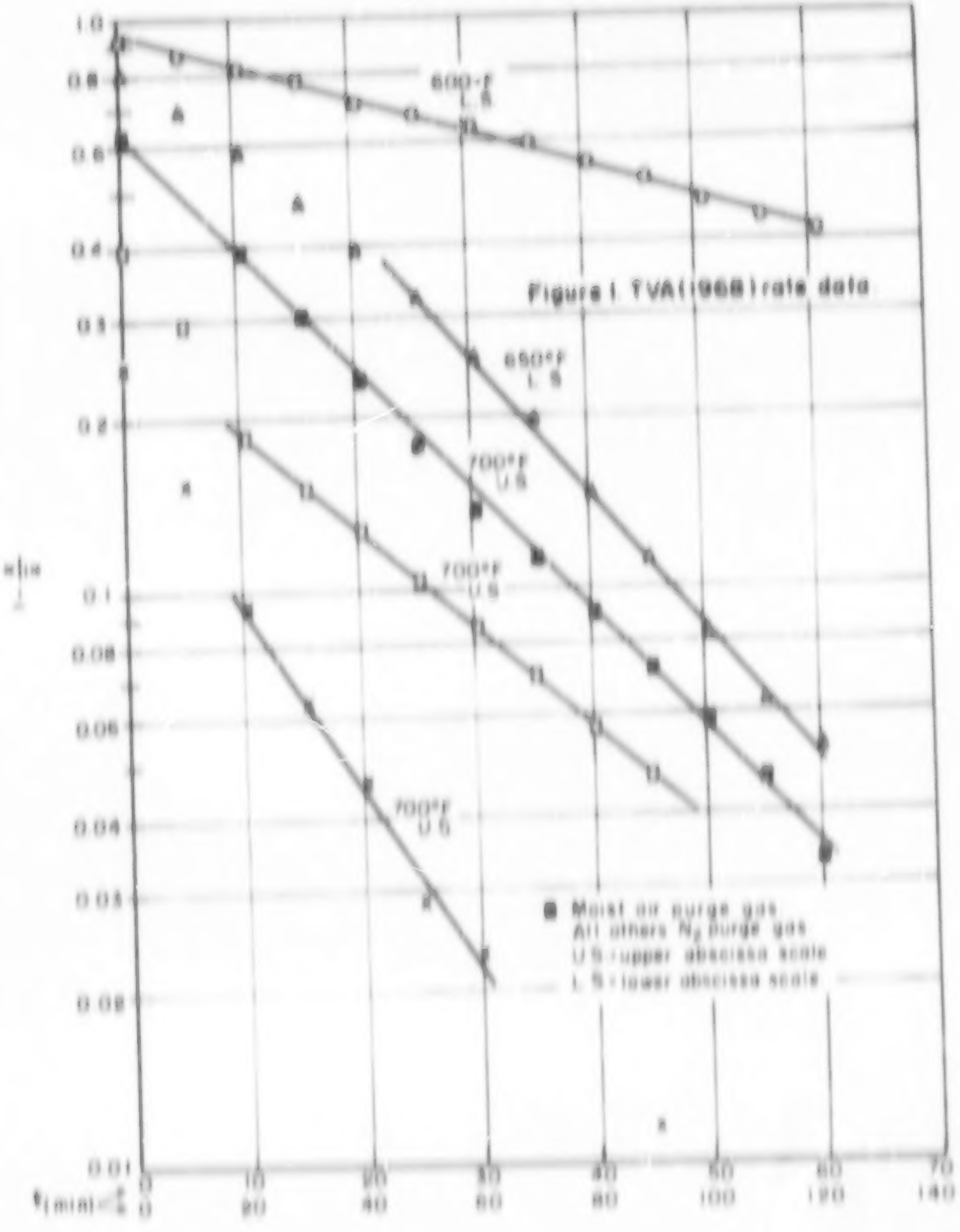


Figure I TVA(1968) rate data

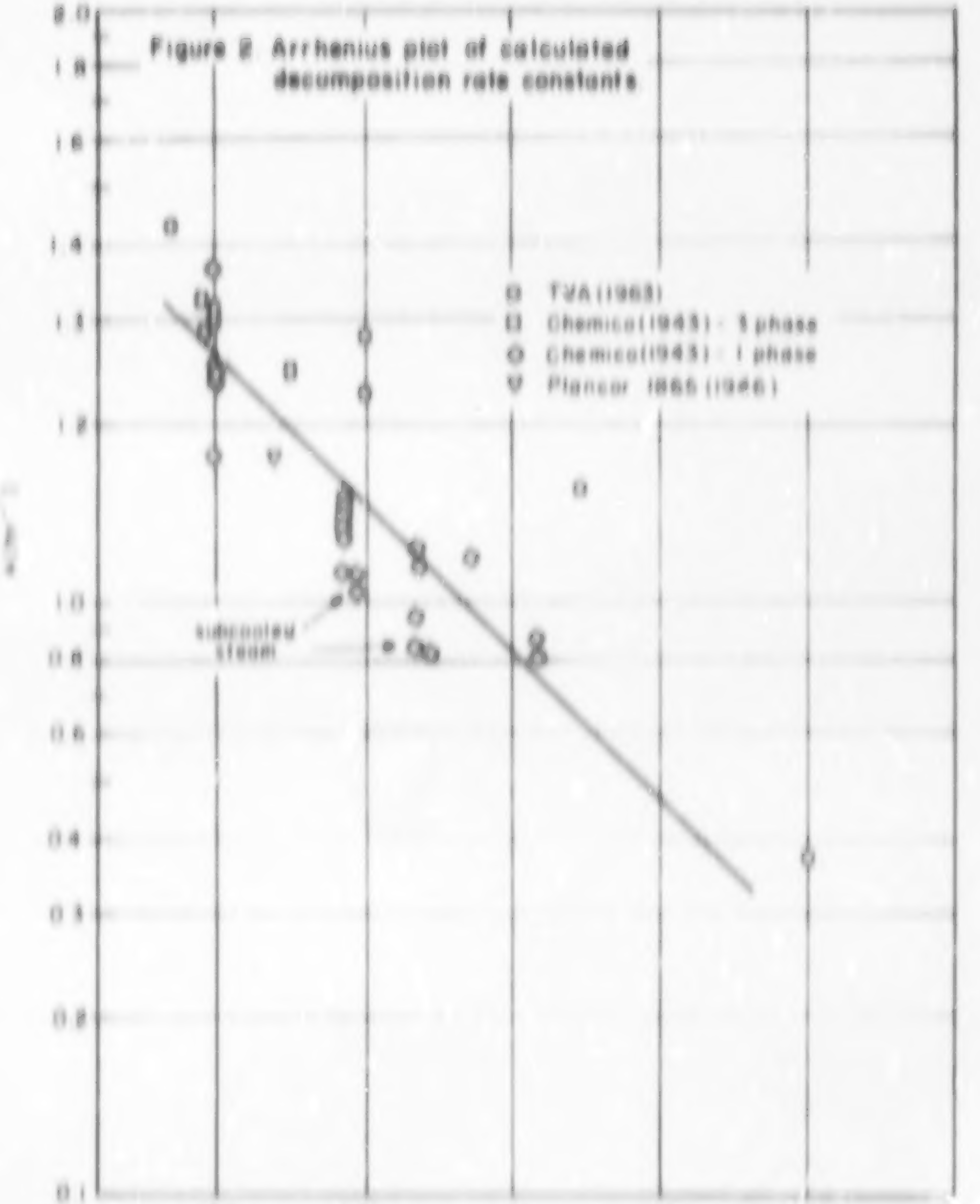


Figure 2 Arrhenius plot of calculated decomposition rate constants

to the proposed reactor operating conditions than do the TVA results; moreover, the points corresponding to runs with steam fed at a temperature close to that of the melt are given the greatest weight. The resulting expression for k(T), which is predicated on the prior assignment of parameter values $y_s$ = 0.01 and $K_s$ = 0.86, has been given as Eq. (2). This formula yields an activation energy for decomposition of 22.5 kcal/g-mole, a figure which can only be regarded as a crude approximation.

A brief literature search turned up three additional references which might contain pertinent kinetic data but are not readily available and require translation. They are as follows:

1. Kuroda, T. and Kondo, H., "Electrolytic Hardening. The Electrolyte," Ōsaka Kōgyō Gijyutsu Shikenjyo Kihō 8, 12 (1957) (In Japanese).
   Heat $H_2SO_4$, $(NH_4)_2SO_4$, $Na_2SO_4$ and $Na_2CO_3$ in electrolytic baths.

2. "Thermal Decomposition of Ammonium Sulfate," German Patent Number 1,151,492 (cl. 12k), July 18, 1963.
   Heat $(NH_4)_2SO_4$, $NH_4HSO_4$ or their solutions to 350° - 650° in the presence of $K_2SO_4$, eventually add steam, to get $H_2SO_4$ and $NH_3$.

3. Rafal' skii, N. G. and Ostrovskaya, L. E., "Kinetics and Mechanism of the Thermal Decomposition of Ammonium Sulfate," Geterogennye Reaktsii i Sposotmost (Minsk: Vyshh Shkola) Sb. 1964, 95-101.
   Data in the temperature range 140°-230°.

### (c) Sublimation of Ammonium Sulfate

The Plancor 1865 report (1946) suggests that at some temperature between 700°F and 750°F as much as 10% of the sulfate fed to the furnace sublimates and passes out of the reactor with the ammonia and exiting steam (see Flow Charts P-2842-0 and P-2844-0) and mention is made of the scaling problems caused by recondensation of this material on the walls of pipes and ducts downstream of the furnace. The 1968 TVA report also notes the occurrence of sublimation, but suggests that this phenomenon is not significant below 700°F. On the other hand, Halstead (1970) found in his studies of the decomposition reaction that no appreciable sublimation occurs at 400°C (751°F), so that this question must be regarded as unresolved. Since something clearly comes off at elevated temperatures, however, it appears reasonable to design the pilot unit to operate at 700°F, with sufficient flexibility being provided to go as high as 750°F to determine the degree to which sublimation takes place at the higher temperatures.

## References

1. Ajax Electric Company Report to Esso Research and Engineering Company entitled "Ammonium Sulfate Decomposition--Electric Furnace Investigation," accompanied by cover letter to Mr. Sheldon Myers dated April 30, 1971.

2. Chemical Construction Company (Chemico) Reports on WPB Research Project NRC-539, Contract WPB-102.
Part I. September 15 to October 31, 1943. (Prepared by E. A. Lof) Part II. November 1 to December 31, 1943. (Prepared by W. B. Lambe)

3. Halstead, W. D., "Thermal Decomposition of Ammonium Sulphate," J. Appl. Chem. 20, 129 (1970).

4. Kiyoura, R. and Urano, K., "Mechanism, Kinetics and Equilibrium of Thermal Decomposition of Ammonium Sulfate," Ind. Eng. Chem. Process Des. Develop. 9, 489 (1970).

5. Plancor 1865 Report (Engineer-Contractors Report on Allumina-from Clay Experimental Plant at Salem, Oregon), 1946.

6. Shell Development Company Report on EPA Contract EHS-D-7145, Task 5, July 28, 1971. Report written by S. H. Garnett and C. H. Deal, accompanied by cover letter to Mr. George M. Newcombe.

7. TVA Report labelled "Applied Research Files" and dated January 5, 1968, prepared by J. E. Jordan and addressed to Mr. Stinson. (Identification as a TVA report by L. I. Griffin--the report itself contains no identification.)

## I. Reaction Kinetics and Reactor Sizing

## Addendum: Evaluation of an Irreversible Reaction Model

June 12, 1974

In the report dated May 30, 1974, reaction rate data for the decomposition of ammonium sulfate were correlated on the basis of a reversible first-order reaction rate law. A request was received from Dr. Griffin of RTI to determine the differences in calculated holdup volumes which would result from an assumption that the decomposition is irreversible. This addendum deals with this question.

Suppose that for the reaction

$$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \qquad (A1)$$

the rate law is

$$r = k_i C$$

where

r = homogeneous decomposition rate of ammonium sulfate, lb-mols/ft³·hr

$k_i$ = first-order rate constant, hr⁻¹

C = concentration of ammonium sulfate in the melt, lb-mols/ft³

The subscript i will be used to denote quantities calculated on the basis of the irreversible rate law.

The space time $\tau_i$ for a continuous salt bath furnace is defined in terms of the melt volume $V_i$ and ammonium sulfate feed rate $q_0$ as

$$\tau_i = \frac{110.4\ V_i\,(ft^3)}{q_0\,(lb/hr)} \qquad (A2)$$

This quantity can be calculated for a given conversion x as

$$\tau_i = \frac{0.99x(1-0.1288x)}{k_i(1-x)} \qquad \text{(A3)}$$

The data given in Table 1 of the May 30 report may be used to obtain values of the rate constant $k_i$ from Eq. (A3), and the resulting values can be plotted on an Arrhenius plot as in Figure 2 of the May 30 report. The data points are highly scattered; a line drawn somewhat arbitrarily through them yields the equation

$$k_i = 1.32\times10^4 \exp[-6204/T(°K)] \qquad \text{(A4)}$$

This expression may be substituted in Eq. (A3), which may then in turn be used to determine the space time $\tau_i$ required to achieve a desired conversion at a temperature T. Once $\tau_i$ is known, the reaction volume $V_i$ for an assumed feed rate $q_0$ can be determined using Eq. (A2).

For illustrative purposes, a feed rate $q_0$ = 3.4 lb$(NH_4)_2SO_4$/min has been assumed, and the reaction volumes required to achieve various conversions have been calculated using both reaction models for a steam to sulfate feed ratio of 0.2 and two temperatures. The results are shown in Figure A1. Two principle results are illustrated by this Figure.

1. The variation of the holdup volume with conversion is approximately the same for both models at low conversions, but as x approaches the equilibrium conversion ($\bar{x}$ = 0.98, calculated from Eq. (4) of the May 30 report) the volume calculated using the reversible model becomes larger than the volume calculated by the irreversible model.

2. At 700°F and relatively low conversions the volumes predicted by both models are approximately the same, but at 750°F the irreversible model predicts a substantially greater required volume. The difference is attributable to the fact that the effective activation energy for k is 22.5 kcal/g-mol (from Eq. (2) in the May 30 report) while that for $k_i$ is 12.3 kcal/g-mol (from Eq. (A4)). Since the values of the rate constants are such that $V = V_i$ at 700°F and since k increases with temperature much faster than does $k_i$, a greater holdup time is required by the irreversible model at 750° to compensate for the relatively low predicted reaction rate at this temperature.

Finally, which model should one believe? The author's preference is for the reversible model, for the following reasons.

1. Experimental evidence that the reaction is in fact reversible is contained in References 4, 6 and 7 of the May 30 report.

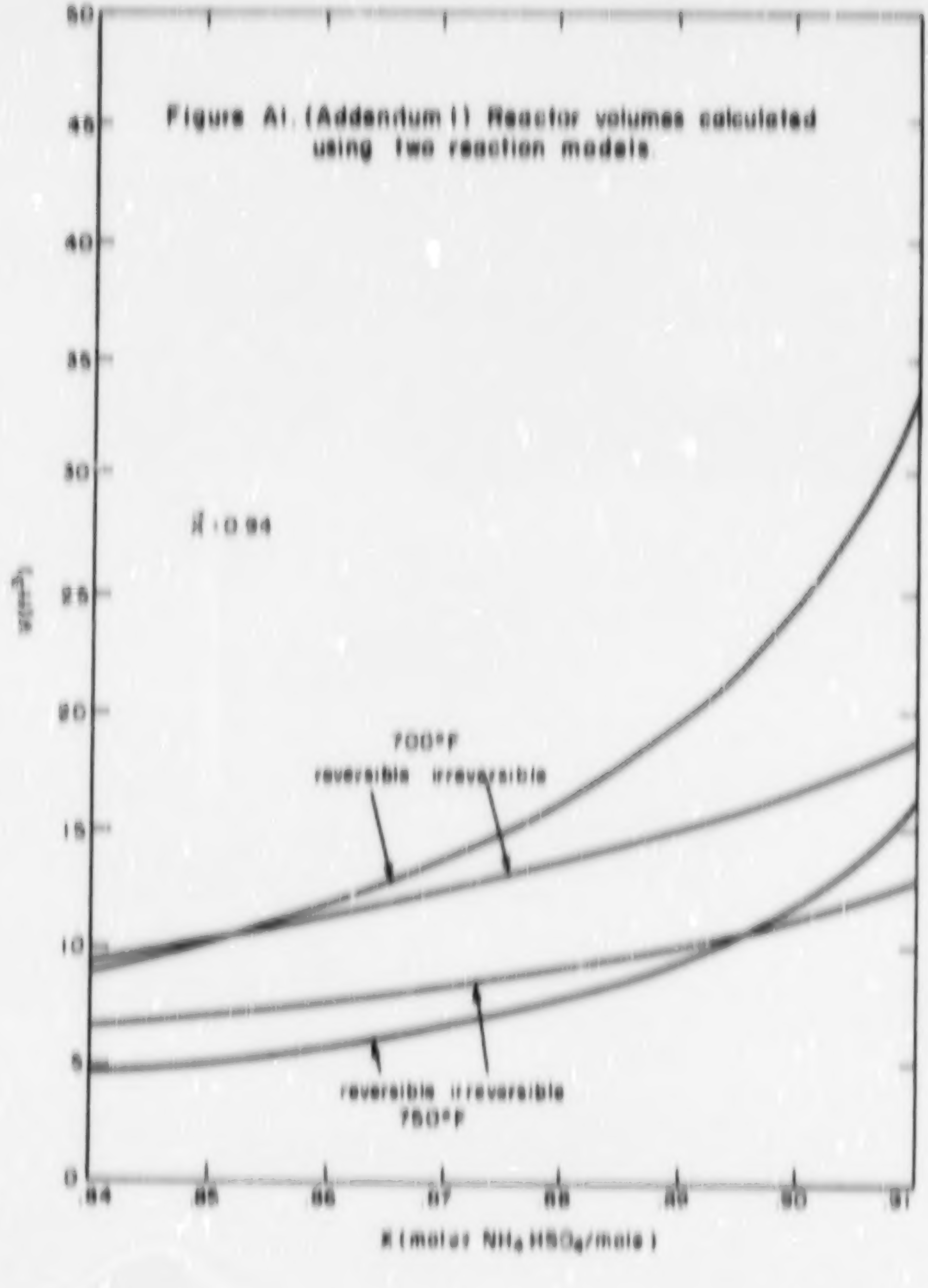


Figure A1 (Addendum I) Reactor volumes calculated using two reaction models

2. Rate constants obtained assuming the reversible reaction model calculated from both batch and continuous reactor data are in reasonable agreement (see Figure 2 of the May 30 report), while the batch data in the TVA report (Reference 7) could not possibly be explained on the basis of an irreversible reaction model.

3. Activation energies for decomposition reactions typically fall in the range 25-60 kcal/g-mol. The effective activation energy obtained using the reversible model--22.5 kcal/g-mol --is not far from this range, while that obtained using the irreversible model--12.3 kcal/g-mol --appears far too low to be credible.

## II. Power Input, Electrode Spacing and Electrode Immersion Depth

June 20, 1974

### INTRODUCTION

In the first phase of this study a rate law was proposed for the decomposition of ammonium sulfate, the parameters of the rate law were determined by analysing available kinetic data, and equations were derived for sizing a continuous salt-bath reactor in which to carry out the decomposition (Felder, 1974). The next phase of the study consisted of the determination of the power input required for a given reactor duty, and the estimation of the electrode spacing and immersion required to yield the calculated power input. The present report outlines the results of these calculations.

The first section of the report summarizes the design equations for a continuous salt bath reactor, including the equations presented in Part I. Subsequent sections outline correlations for power input and electrode spacing, and summarize the data used to derive these correlations.

## SUMMARY OF DESIGN EQUATIONS

The reaction

$$(NH_4)_2SO_4 \rightleftarrows NH_4HSO_4 + NH_3 \qquad (1)$$

is to be carried out in a continuous single-phase electrolytic salt-bath furnace, with superheated steam being bubbled through the melt. Let

$T$ = reactor temperature, °K

$\gamma$ = ratio of steam feed rate to ammonium sulfate feed rate, lb $H_2O$/lb $(NH_4)_2SO_4$

$T_s$ = inlet steam temperature, °K

$T_0$ = inlet feed temperature, °K

$x$ = mol fraction of ammonium bisulfate in the melt

$q_a$ = ammonium sulfate feed rate, lb/min.

Calculate

$$k(\text{hr}^{-1}) = 6.22 \times 10^7 \exp[-11{,}320/T] \qquad (2)$$

$$\bar{x} = \frac{[0.185(7.333\gamma-1)^2 + 6.307\gamma]^{1/2} - 0.43}{(7.333\gamma - 1)} \qquad (3)$$

$$\tau(\text{hr}) = \frac{0.99\,x\,(1-0.1288x)}{k(\bar{x}-x)} \qquad (4)$$

$$V(\text{ft}^3) = 0.5435\, q_a\, \tau \qquad (5)$$

where k is a first-order decomposition rate constant, $\bar{x}$ is the equilibrium conversion at the given reaction conditions, $\tau$ is the reactor space time, and V is the melt volume. If the inner diameter of the bed D (inches) and the electrode diameter $d_e$ (inches) are specified, the melt depth h can be calculated as

$$h(\text{in}) = \frac{6912V}{\pi(D^2-2d_e^2)} \qquad (6)$$

The useful power, or power required to bring the sulfate feed to the reaction temperature ($P_1$), plus that required to bring the steam to the reaction temperature ($P_2$), plus that absorbed by the endothermic reaction ($P_3$) is calculated as follows:

$$P_1(\text{kW}) = 0.2398\, q_a[H(T) - H(T_0)] \qquad (6a)$$

$$\cong q_0 \left[5.94 \times 10^{-3} (T - T_0) + 8.057 \times 10^{-6} (T^2 - T_0^2)\right] \qquad (6b)$$

The specific enthalpies of ammonium sulfate $H(T)$ and $H(T_0)$ (kcal/g-mol) may be read from Figure 1a.

$$P_2(\mathrm{kW}) = q_0 \gamma \left[0.01232\ (T - T_0) + 2.184 \times 10^{-6} (T^2 - T_0^2)\right] \qquad (7)$$

$$P_3(\mathrm{kW}) = 0.2398\ q_0 x \Delta H_r (T) \qquad (8a)$$

$$\cong q_0 x \left[6.865 - 3.81 \times 10^{-3} T + 1.64 \times 10^{-6} T^2 + \frac{9.54}{T}\right] \qquad (8b)$$

The heat of reaction $\Delta H_r$ (T) kcal/g-mol) may be read from Figure 1b.

$$P_u(\mathrm{kW}) = P_1 + P_2 + P_3 \qquad (9)$$

The total power input is the sum of $P_u$ and the heat loss from the reactor. If an efficiency $\eta$ is defined as the ratio of useful power $P_u$ to total power $P = P_u + P_L$, then

$$P = \frac{P_u}{\eta} \qquad (10)$$

In tests on a reactor of the approximate size of the proposed pilot plant unit (Chemico, 1943) the efficiency was approximately 0.7; this figure may be substituted in Eq. (10) in the absence of more definitive data.

Next, define

E = voltage across electrodes, volts

Im = electrode immersion depths, inches

℄L = centerline distance between electrodes, inches

An approximate correlation between the voltage, electrode spacing, immersion depth, and power input to the reactor is

$$\frac{E^2 Im^{0.88}}{(℄L - d_e)} = \frac{P}{0.116} \qquad (11)$$

Two of the variables Im, E and ℄L may be specified, and the third may then be calculated from Eq. (11) using the calculated value of P. The choices of ℄L and Im must be consistent with the values of the reactor diameter and melt depth specified previously.

Sample Design Calculation

Ammonium sulfate is to be decomposed at 700°F ($T$ = 644.4°K) with $\gamma$=0.2 lb $H_2O$/lb $(NH_4)_2SO_4$. The feed rate is $q_0$ = 3.4 lb

$(NH_4)_2SO_4$/min, and a conversion $x = 0.667$ is desired (corresponding to 35 weight percent bisulfate in the product). From Eqs. (2)-(5),

$k = 1.46\ hr^{-1}$

$\bar{N} = 0.94$ mols $NH_4HSO_4$/mol

$\tau = 7.15$ hr

$V = 13.2\ ft^3$

Suppose that a 3 ft ID bath and 6-in diameter electrodes are used. From Eq. (6), the melt depth is then

$h = 23.7$ inches

Next suppose that the sulfate enters at 140°F ($T_0$ = 333.3° K), and the steam enters at 650°F ($T_s$=616.7°K). From Eqs. (6)-(9)

$P_1 = 14.6$ kW (energy to heat the sulfate)

$P_2 = 0.3$ kW (energy to heat the steam)

$P_3 = 21.6$ kW (energy absorbed by the reaction)

$P_u = 36.5$ kW

If an efficiency of 70% is assumed, the total required power input is from Eq. (10)

$P = 52.1$ kW

Let us say arbitrarily that a voltage of 40 volts is applied ($E=40$), and that the electrodes are set with their centers five inches from the wall on opposite ends of a diameter, so that ¢L = 26 in. Then from Eq. (11)

$$Im^{.56} = \frac{52.1(26-6)}{.116(40)^2} = 5.614$$

from which

$Im = 21.8$ inches

Since the melt depth was calculated to be 23.7 in, this electrode immersion is acceptable. The results are summarized below:

Bath ID = 36 inches

Melt depth = 23.7 inches ≈ 24 inches

Voltage = 40 volts

Electrode centerline distance = 26 inches

Electrode immersion depth = 21.8 inches ≈ 22 inches

Finally, let us consider the variations in electrode placement which would be required for a constant power input if different voltages were applied. Since the values of Im and ¢L calculated for E=40 volts are close to the limits imposed by the reactor inner diameter and the melt depth, we will rule out for convenience any further increases in these variables. An increase in E above 40 volts must therefore be compensated for by a decrease in Im, and a decrease in E must be balanced by a decrease in ¢L. Results for three voltages are given below:

P = 52.1 kW, E = 30 volts → Im = 21.8 inches, ¢L = 17.1 inches
P = 52.1 kW, E = 40 volts → Im = 21.8 inches, ¢L = 26.0 inches
P = 52.1 kW, E = 50 volts → Im = 9.8 inches, ¢L = 26.0 inches

The sections that follow outline the derivations of the given equations for input power and electrode spacing and immersion.

## POWER INPUT REQUIREMENT

The reaction

$$(NH_4)_2SO_4 \overset{steam}{\rightleftarrows} NH_4HSO_4 + NH_3 \qquad (12)$$

is to be carried out in a continuous salt bath reactor. An energy balance may be written as follows:

$$P = P_1 + P_2 + P_3 + P_L \qquad (13)$$

where

$P$ = total energy input to the reactor

$P_1$ = energy required to raise the ammonium sulfate feed to the melt temperature

$P_2$ = energy required to bring the entering steam to the melt temperature

$P_3$ = energy absorbed by the reaction

$P_L$ = heat loss to the reactor surroundings

It is assumed that no decomposition of ammonium bisulfate takes place, and that sublimation of ammonium sulfate can be neglected.

## Heating of Ammonium Sulfate

Suppose $q_0$ lb $(NH_4)_2SO_4$/min enter the reactor at a temperature $T_0$(°K), and that the melt temperature is T(°K). Then (letting A stand for $(NH_4)_2SO_4$)

$$P_1(\text{kW}) = q_0 \frac{\text{lb A}}{\text{min}} \left| \frac{454\ \text{g-mols}}{132\ \text{lb A}} \right| \frac{\Delta H_1\ \text{kcal}}{\text{g-mol}} \left| \frac{60\ \text{min}}{\text{hr}} \right| \quad (14)$$

$$\frac{1.162\times10^{-3}\ \text{kW·hr}}{\text{kcal}} = 0.2398\ q_0\ \Delta H_1$$

where $\Delta H_1 = H(T) - H(T_0)$ equals the enthalpy change in kcal when 1 g-mol of ammonium sulfate goes from $T_0$(°K) to T (°K).

Kelley et al. (1946) measured the enthalpy content of $(NH_4)_2SO_4$ from 300°K to 600°K. A plot of the results is shown as the solid curve of Figure 1a; $\Delta H_1$ can be obtained from this graph as $[H(T) - H(298.16)] - [H(T_0) - H(298.16)]$.

Shomate and Naylor (1945) present an empirical expression for the curve of Figure 1a:

$$[H(T) - H(298.16)](\text{kcal/g-mol}) = 0.02477T + 3.36\times10^{-5}T^2 - 10.372 \quad (15)$$

The dashed curve of Figure 1a shows this function at temperatures above 600°K. $\Delta H_1$ may be calculated using Eq. (15), and the resulting expression may be substituted into Eq. (14) to yield

$$P_1(\text{kW}) = q_0[5.94\times10^{-3}(T-T_0) + 8.057\times10^{-6}(T^2 - T_0^2)] \quad (16)$$

which is the expression of Eq. (6b).

## Heating or Cooling of Steam

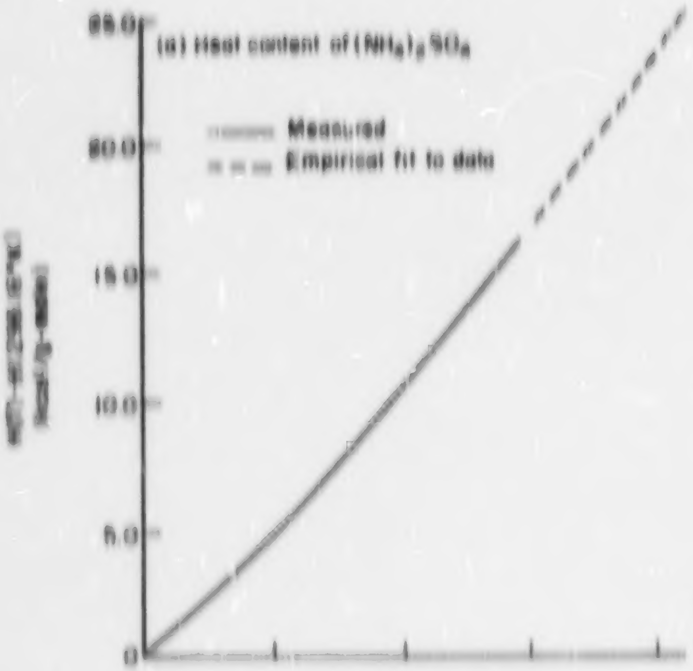
If $\gamma$ is the mass ratio of steam to ammonium sulfate fed, then the energy required to bring the steam from its inlet temperature $T_s$(°K) to the melt temperature T is

$$P_2(\text{kW}) = q_0\gamma \frac{\text{lb}\ H_2O}{\text{min}} \left| \frac{454\ \text{g-mols}\ \ H_2O}{18\ \text{lb}\ H_2O} \right| \frac{\Delta H_2\ \text{kcal}}{\text{g-mol}} \left| \frac{60\ \text{min}}{\text{hr}} \right|$$

$$\frac{1.162\times10^{-3}\ \text{kW·hr}}{\text{kcal}}$$

$$= 1.758\ q_0\gamma\ \Delta H_2 \quad (17)$$

The heat capacity of steam is (Himmelblau, 1967)



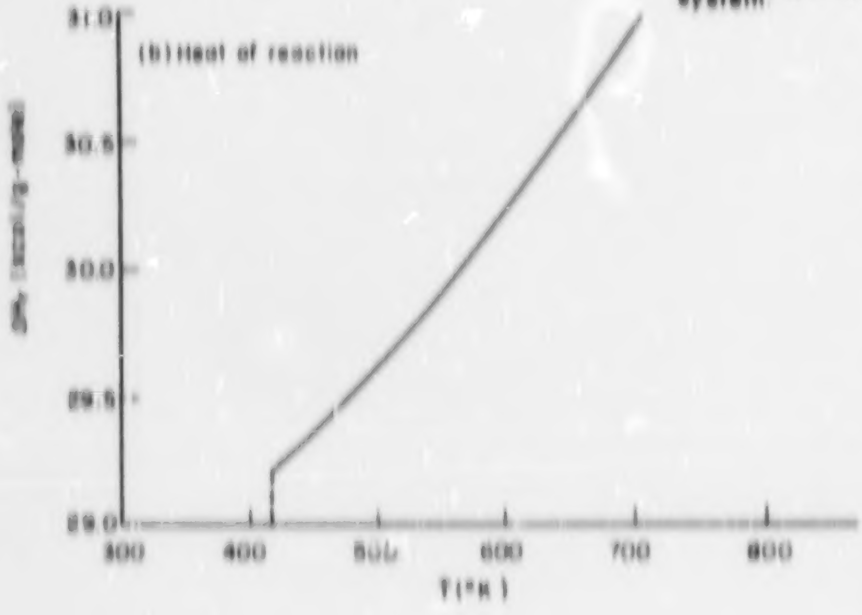


Figure I (Part II)
Enthalpy vs temperature for $(NH_4)_2SO_4$-$NH_4HSO_4$ system

$$C_{ps}(\text{cal/g-mol}\cdot{}^{\circ}\text{K}) = 7.836 + 0.0032T \qquad (18)$$

This expression divided by 1000 cal/kcal may be integrated from $T_m$ to T to yield $\Delta H_s$, which may in turn be substituted into Eq. (17). The result is

$$P_s(\text{kW}) = q_a y[0.01232(T - T_m) + 2.184 \times 10^{-6}(T^2 - T_m^2)] \qquad (19)$$

which is Eq. (7).

## Heat of Reaction

Suppose x(moles $NH_4HSO_4$/mols total) is the mol fraction of bisulfate in the melt. If sublimation of ammonium sulfate is neglected, x also represents the mols of ammonium sulfate which react per mol fed. The energy absorbed by the reaction is therefore

$$P_r(\text{kW}) = \frac{q_a \text{ lb A fed}}{\text{min}}\Bigg|\frac{454 \text{ g-mols A}}{132 \text{ lb A}}\Bigg|\frac{x \text{ mols react}}{\text{mol fed}}\Bigg|$$

$$\frac{\Delta H_r \text{ kcal}}{\text{g-mol}}\Bigg|\frac{60 \text{ min}}{\text{hr}}\Bigg|\frac{1.162\times10^{-3} \text{ kW}\cdot\text{hr}}{\text{kcal}}$$

$$= 0.2398\, q_a\, x\, \Delta H_r \qquad (20)$$

Kelley et. al. (1946) calculated the heat of reaction as a function of temperature. A plot of the results is shown in Figure 1b; the lower limit of the curve -- T = 417°K -- is the freezing point of ammonium bisulfate. The value of $\Delta H_r$ at the reaction temperature T may be read directly from Figure 1b and substituted into Eq. (20).

The same authors derived an expression which fits $\Delta H_r(T)$ over the entire range shown on Figure 1b:

$$\Delta H_r(T) = 28.63 - 1.59 \times 10^{-2}\, T + 6.85 \times 10^{-6} T^2 + \frac{39.8}{T} \qquad (21)$$

This expression may be substituted into Eq. (20) to yield

$$P_r(\text{kW}) = q_a\, x\, [6.865 - 3.81 \times 10^{-3} T + 1.64 \times 10^{-6}\, T^2 + \frac{9.54}{T}] \qquad (22)$$

which is Eq. (8b).

Power input data are available for two ammonium sulfate decomposition reactors (Chemico, 1963). The data are summarized in Table 1.

TABLE 1. CHEMICO (1943) POWER DATA

| T(°F) | E(volts) | ‡L(") | †Dp(") | P(kw) | $P_c$(kw) | $P_u$(kw)[1] | $\eta = P_u/P$ |
|---|---|---|---|---|---|---|---|
| ***720 | 79 | 36 | 19.5 | 402 | 414 | 272 | 0.67 |
| ***745 | 80 | 36 | 19.5 | 427 | 421 | 296 | 0.69 |
| ***740 | 81 | 36 | 25.5 | 507 | 499 | 402 | 0.79 |
| ***740 | 77 | 48 | 31.5 | 444 | 433 | 427 | 0.96 |
| ***740 | 80 | 48 | 31.5 | 463 | 457 | 358 | 0.77 |
| ***760 | 80 | 48 | 31.5 | 446 | 457 | 316 | 0.71 |
| ***740 | 91 | 46 | 31.5 | 552 | 548 | 438 | 0.79 |
| ***745 | 90 | 48 | 31.5 | 537 | 539 | 429 | 0.80 |
| *740 | 45.5 | - | - | 75 | 75 | 46 | 0.61 |
| *740 | 45.5 | - | - | 72 | 75 | 45 | 0.63 |
| *735 | 45.7 | - | - | 72 | 76 | 45 | 0.63 |
| *735 | 45.7 | - | - | 71 | 76 | 45 | 0.63 |
| *675 | 45.5 | - | - | 82 | 75 | 72 | 0.88 |
| *665 | 45.5 | - | - | 78 | 75 | 68 | 0.87 |
| *660 | 45.5 | - | - | 75 | 75 | 69 | 0.92 |
| *690 | 45.0 | - | - | 74 | 74 | 58 | 0.78 |
| *690 | 39.0 | - | - | 51 | 55 | 41 | 0.81 |
| *585 | 39.0 | - | - | 56 | 55 | 41 | 0.73 |
| *685 | 39.0 | - | - | 56 | 55 | 41 | 0.73 |
| *705 | 45.5 | - | - | 78 | 75 | 58 | 0.74 |
| *705 | 45.5 | - | - | 75 | 75 | 54 | 0.72 |
| *705 | 45.5 | - | - | 75 | 75 | 58 | 0.77 |

***3-phase reactor. $P_c$ calculated from Eq. (26).

*1-phase reactor. $P_c$ calculated from Eq. (23), assuming 6-inch electrodes. ‡ L = 28 inches.

†Dp = 22 inches

[1] Useful power, calculated from Eqs. (6) - (9).

TABLE 11. ENGLISH-TO-METRIC UNIT CONVERSIONS

| Variable | Metric Equivalent | Conversion |
|---|---|---|
| Pound (lb) | kilogram (kg) | M(kg) = 0.4536 M(lb) |
| Foot (ft) | Meter (m) | L(m) = 0.3048 L(ft) |
| Cubic Foot ($ft^3$) | Liter (l) | $V_{(l)}$ = 28.32 V($ft^3$) |

Figure 3 shows a plot of the total power input P vs. the useful power $P_u = P_s + P_d + P_a$ calculated using Eqs. (14), (17) and (22). The vertical distance from each point to the 45°line provides a measure of the heat loss. Also shown is a single point for a large pilot plant reactor described in the Plancor 1865 report (1946).

The reactor efficiency $\eta = P_u/P$ averages 0.7-0.8 for both the small single-phase and larger three-phase reactors. The lower figure may be taken as a basis for the design of a small pilot plant unit, anticipating that the percentage heat loss will decrease as the reactor size increases.

## CORRELATION OF POWER, VOLTAGE, AND ELECTRODE SPACING AND IMMERSION DEPTH

In determining a correlation between electrode spacing, input voltage and input power, four sources of data were available: two were studies on small single-phase reactors in the 3-80 kW range, and the other two involved larger three-phase reactors with power inputs above 250 kW. It had been hoped that a single correlation could be obtained for all four data sets, but this was not possible. The pilot plant reactor whose design is the ultimate objective of this study will have a power requirement in the first, lower range; however, should the process prove to be commercially feasible reactors in the higher power range will be required. For this reason the correlations derived for both the small and large reactors are reported in this study.

Let

E = voltage across the electrodes, volts
Im = immersion depth of electrodes, inches
℄L = distance between electrode centerlines (1 phase - 2 electrodes)
= diameter of circle through electrode centerlines (3 phase - 3 electrodes)
$d_e$ = electrode diameter, inches
P = power input, kW

Two sources of data were available which could be used to establish a correlation among these variables: the Chemico (1943) reports and an Ajax Electric Company report (1971). The derived correlations are summarized below.

1. Ajax Company Reactor

Rectangular bath: single-phase, two electrodes
Electrode diameter: 6 inches
Power range: 3.5 kW - 53 kW

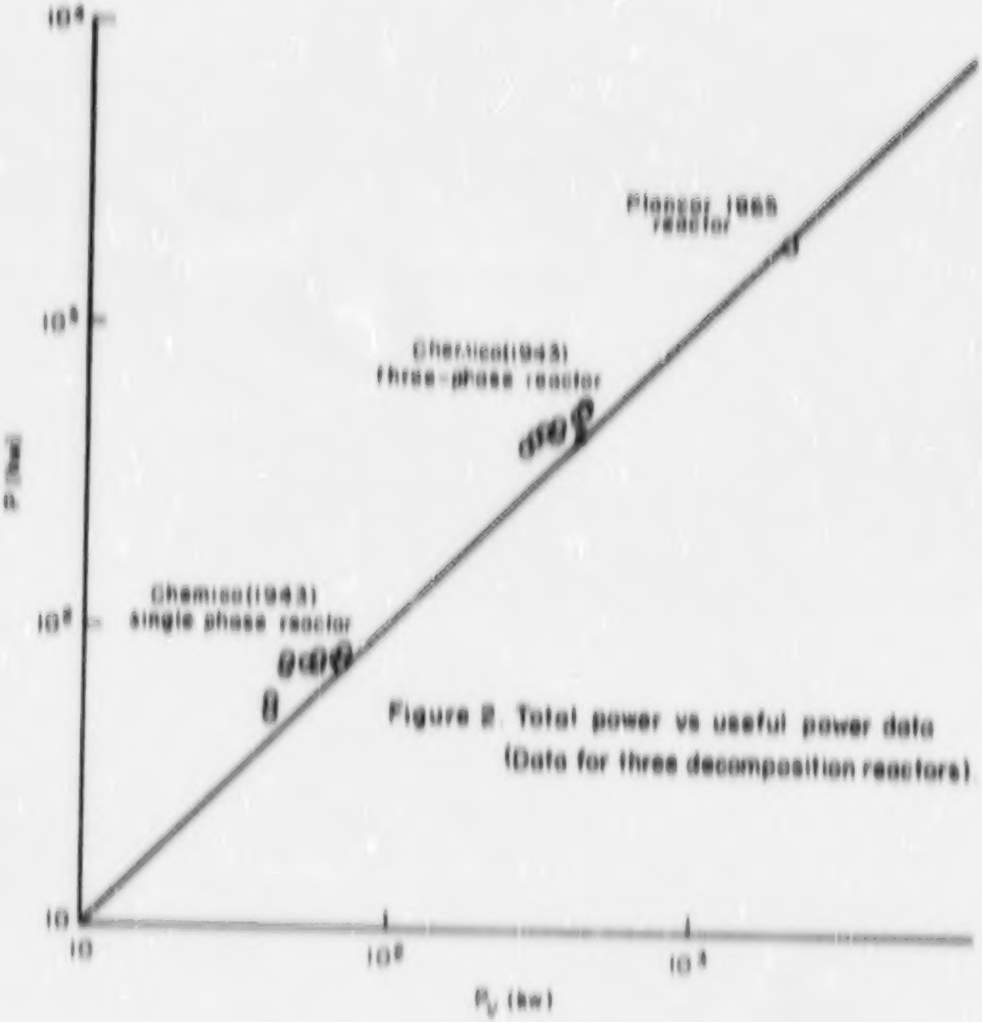


Figure 2. Total power vs useful power data
(Data for three decomposition reactors)

Voltage range: 16.6 volts - 37.5 volts
Centerline distance: 10 inches - 23 inches
Immersion depth: 10 inches - 20 inches

Correlations:

$$P = 0.042E^2(Im)^{0.88}\ (\text{℄}L - d_e)^{-1} \qquad \text{℄}L > 17 \text{ inches} \qquad (23)$$
$$P = 0.22E^2(Im)^{0.88}\ (\text{℄}L)^{-1.59} \qquad \text{℄}L \leq 17 \text{ inches} \qquad (24)$$

The data used to obtain these correlations were obtained using a melt containing approximately 15% ammonium sulfate and 85% ammonium bisulfate and ammonium pyrosulfate, and no steam. The melt composition changed during the course of each run, adding a note of uncertainty to the results.

2. Single-Phase Chemico Reactor with Steam

Cylindrical bath: single phase, two electrodes
Electrode diameter: uncertain - guess 6 inches
Power range: 50-80 kW
Voltage range: Most runs at 45.5 volts, three runs at 39 volts
Centerline distance: unknown - guess 28 inches
Immersion depth: unknown - guess 22 inches

Correlation:

$$P = 0.116E^2\ Im^{0.88}\ (\text{℄}L - d_e)^{-1} \qquad (25)$$

Values of the measured power and the power predicted using this correlation are listed in Table 1.

The size and operating conditions of this reactor come closer to those of the proposed pilot plant unit than do those of any of the others reported on, but unfortunatly the data for this unit are completely inadequate for the independent determination of a correlation. The exponents of Im and ($\text{℄}L-d_e$) in Eq. (25) were taken from the Ajax correlation for lack of any other basis for the choice. The exponent of Im is probably a reasonable value, but that of the quantity ($\text{℄}L - d_e$) is highly suspect in view of the differences in reactor geometries between the Ajax and Chemico systems.

3. Three-Phase Chemico Reactor

Cylindrical bath: three phase, three electrodes
Electrical diameter: 12 inches
Power range: 400-500 kW
Voltage range: most runs between 77 and 81 volts, two runs at 90-91 volts
Centerline distance: 36 inches - 48 inches
Immersion depth: 19.5 inches - 31.5 inches

Correlation:

$$P = 0.747 E^{1.5}\, Im^{0.97}\, (\ell L - d_s)^{-0.47} \qquad (26)$$

Measured and predicted values of P are listed in Table 1. A correlation which forced the exponent of the voltage to be 2.0 was attempted, but the fit was not particularly good.

In the Plancor 1865 report (1946) and in material related to it data are given on a large three-phase decomposition reactor. Estimates of the parameters are as follows:

$$P = \frac{350 \text{ kWh}}{\text{ton}} \left| \frac{550 \text{ tons}}{4 \text{ day}} \right| \frac{1 \text{ day}}{24 \text{ hr}} = 2005 \text{ kW}$$

$d_s$ = 20 inches
$E$ = 113 volts
$\ell L$ = 72 inches
$Im$ = 44 inches

$\left.\begin{matrix} E = 113 \text{ volts} \\ \ell L = 72 \text{ inches} \\ Im = 44 \text{ inches} \end{matrix}\right\}$ highly speculative

If the values of $d_s$, E, $\ell L$ and Im are substituted into Equation (26), a power input of 755 kW is predicted, compared to a measured value of 2005 kW. This agreement is unsatisfactory; however, there is presently no way to determine how much of the discrepancy stems from the correlation and how much is due to incorrect information about the Plancor reactor.

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# APPENDIX H

# COST ESTIMATES FOR VARIOUS FLUE GAS DESULFURIZATION PROCESSES

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TABLE B-1. AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION - SULFURIC ACID PRODUCTION

SUMMARY OF ESTIMATED FIXED INVESTMENT[a]

([illegible]-MW new coal-fired power unit, [illegible] S in fuel, dry basis; [illegible] $SO_2$ removal)

| | Investment, $ | Percent of subtotal direct investment |
|---|---|---|
| Makeup handling and preparation (storage tank, pumps, and vaporizer) | 170,000 | 1.1 |
| Particulate scrubbing (particulate scrubber, pumps, sump, surge tanks, agitators, soot blowers, and neutralization system) | [illegible] | 11.8 |
| Sulfur dioxide absorption (sulfur dioxide absorbers, entrainment separators, sump, surge tanks, pumps, and soot blowers) | [illegible] | [illegible] |
| Reheat (reheaters and soot blowers) | [illegible] | 3.9 |
| Flue gas handling (fans and duct work) | [illegible] | [illegible] |
| Ammonia regeneration (weigh feeders, electrical thermal decomposer, condenser, ammonia stripper, surge tanks, ammonia absorber, absorber offgas fan, pumps) | [illegible] | [illegible] |
| Sulfur dioxide regeneration (solution storage tanks, drum flaker, belt conveyors, acidulator, agitator, fan, sulfur dioxide stripper, surge tanks, pumps, purge treatment system) | [illegible] | 5.9 |
| Slurry processing (evaporator-crystallizer,[b] offgas ejector, pumps, cyclone concentrator, centrifuge, surge tanks, condensate tank, desuperheater) | [illegible] | [illegible] |
| Cake processing (cake conveyor, steam/air heater, dryer, cyclone dust collector, fabric filter dust collectors, dryer fan, belt conveyors, bucket elevator, storage bin, vibrators, surge bin and dust fan) | [illegible] | [illegible] |
| Sulfuric acid production unit | [illegible] | [illegible] |
| Acid storage and shipping (storage tank and pumps for one month's production of acid) | [illegible] | 1.1 |
| Utilities (instrument air generation and supply, and distribution systems for process steam, water, and electricity) | [illegible] | [illegible] |
| Services (buildings, shops, stores, site development, roads, railroads, and walkways) | [illegible] | [illegible] |
| Construction facilities | [illegible] | [illegible] |
| Subtotal direct investment | [illegible] | [illegible] |
| Engineering design and supervision | [illegible] | 11.0 |
| Construction field expense | [illegible] | 11.0 |
| Contractor fees | [illegible] | [illegible] |
| Contingency | [illegible] | [illegible] |
| Subtotal fixed investment | [illegible] | [illegible] |
| Allowance for startup and modifications | [illegible] | [illegible] |
| Interest during construction ([illegible]/annum rate) | [illegible] | [illegible] |
| Subtotal capital investment | [illegible] | [illegible] |
| Land ([illegible] acres) | [illegible] | [illegible] |
| Working capital | [illegible] | [illegible] |
| Total capital investment | [illegible] | [illegible] |

a. Basis:
Stack gas reheat to [illegible]°F by indirect steam reheat.
Midwest plant location, average cost basis mid-[illegible].
Investment requirements for disposal of flyash excluded.

b. Double effect evaporator-crystallizer.

## TABLE B-1A. AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION - SULFURIC ACID PRODUCTION

## TOTAL AVERAGE ANNUAL REVENUE REQUIREMENT - - REGULATED UTILITY ECONOMICS[a]

(500-MW new coal-fired power unit, 3.5% S in fuel; dry basis; 90% $SO_2$ removal)

| | Annual quantity | Unit cost, $ | Total annual cost, $ | Percent of net annual rev. req. |
|---|---|---|---|---|
| **Direct costs** | | | | |
| Delivered raw material | | | | |
| Ammonia, anhydrous | 6,270 tons | 150/ton | 940,500 | 7.86 |
| Catalyst | 1,800 liters | 1.65/liter | 3,000 | 0.03 |
| Subtotal raw material cost | | | 943,500 | 7.89 |
| Conversion costs | | | | |
| Operating labor and supervision | 45,900 man-hr | 8.00/man-hr | 367,200 | 3.07 |
| Utilities | | | | |
| Steam | 738,100 MM Btu | 1.50/MM Btu | 1,107,200 | 9.25 |
| Process water | 4,389,100 K gal | 0.03/K gal | 131,700 | 1.10 |
| Demineralized water | 11,131 K gal | 0.45/K gal | 5,000 | 0.04 |
| Electricity | 151,735,000 kWh | 0.029/kWh | 3,397,000 | 28.38 |
| Maintenance, 6% of direct investment (labor and material) | | | 1,565,800 | 13.07 |
| Analyses | | | 43,000 | 0.36 |
| Subtotal conversion costs | | | 6,614,400 | 55.26 |
| Subtotal direct costs | | | 7,557,900 | 63.15 |
| **Indirect costs** | | | | |
| Capital charges | | | | |
| Depreciation, interim replacement, and insurance at 3.6% of total capital investment less land and working capital | | | 1,895,900 | 15.84 |
| Average cost of capital and taxes at 8.6% of total capital investment | | | 4,536,500 | 37.90 |
| Overhead | | | | |
| Plant, 50% of conversion costs | | | 1,315,400 | 10.99 |
| Administrative, 10% of operating labor | | | 36,700 | 0.31 |
| Marketing, 10% of sales revenue | | | 375,700 | 3.14 |
| Subtotal indirect costs | | | 8,160,200 | 68.18 |
| Gross annual revenue requirements | | | 15,718,100 | 131.33 |
| **Byproduct sales revenue** | | | | |
| Ammonium sulfate | 22,175 tons | 45/ton | (975,500) | (8.15) |
| Sulfuric acid (98%) | 92,450 tons | 30/ton | (2,773,700) | (23.18) |
| Subtotal byproduct sales revenue | | | (3,749,200) | (31.33) |
| Net annual revenue requirements | | | 11,968,900 | 100.00 |

| | Dollars/ton coal burned | Mills/kWh | Cents/million Btu heat input | Dollars/long ton sulfur removed |
|---|---|---|---|---|
| Equivalent net unit revenue requirement | 7.91 | 3.42 | 38.00 | 281.35 |

---

a. Basis:
Remaining life of power plant, 30 yr.
Coal burned, 1,512,500 tons/yr, 9,000 Btu/kWh.
Stack gas reheat to 175°F by indirect steam reheat.
Power unit onstream time, 7,000 hr/yr.
Midwest plant location, 1980 revenue requirements.
Total capital investment, $52,750,000; direct investment, $26,097,000.
Investment and revenue requirement for disposal of flyash excluded.

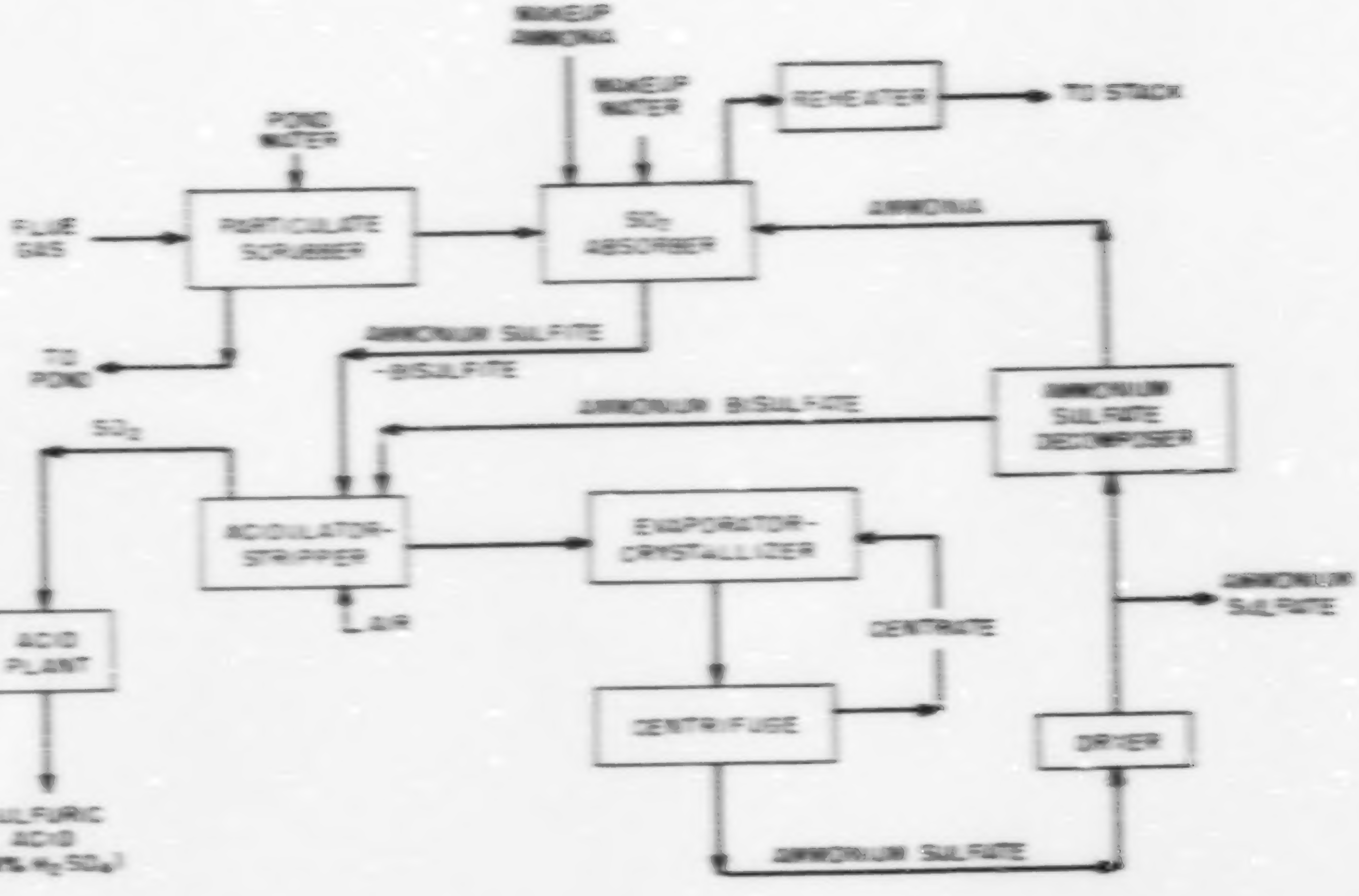
FLUE GAS
POND WATER
PARTICULATE SCRUBBER
TO POND
MAKEUP AMMONIA
MAKEUP WATER
$SO_2$ ABSORBER
REHEATER
TO STACK
AMMONIA
AMMONIUM SULFITE -BISULFITE
AMMONIUM BISULFATE
AMMONIUM SULFATE DECOMPOSER
$SO_2$
ACIDULATOR-STRIPPER
AIR
ACID PLANT
SULFURIC ACID (98% $H_2SO_4$)
EVAPORATOR-CRYSTALLIZER
CENTRATE
CENTRIFUGE
AMMONIUM SULFATE
DRYER
AMMONIUM SULFATE

Figure H-1. Ammonia absorption–ammonium bisulfate regeneration process–sulfuric acid production.

## TABLE H-2. AMMONIA ABSORPTION - SCRUBBING LIQUORS SATURATED WITH AMMONIUM SULFATE - AMMONIUM SULFATE PRODUCTION

## SUMMARY OF ESTIMATED FIXED INVESTMENT[a]

(500-MW new coal-fired power unit, 3.5% S in fuel; Dry basis; 90% $SO_2$ removal)

| | Investment, $ | Percent of subtotal direct investment |
|---|---|---|
| Makeup handling and preparation (storage tank, pumps, and vaporizer) | 1,275,000 | 6.5 |
| Particulate scrubbing (particulate scrubber, pumps, sump, surge tanks, agitators, soot blowers, and neutralization system) | 3,091,000 | 15.9 |
| Sulfur dioxide absorption (sulfur dioxide absorbers, entrainment separators, sump, surge tanks, pumps, and soot blowers) | 6,175,000 | 31.7 |
| Reheat (reheaters and soot blowers) | 1,003,000 | 5.1 |
| Flue gas handling (fans and duct work) | 3,339,000 | 17.1 |
| Ammonia sulfate production (tanks, pumps, agitators, oxidizer, air compressor, cooler, and purge treatment) | 635,000 | 3.3 |
| Slurry processing (evaporator-crystallizer,[b] offgas ejector, pumps, cyclone concentrator, centrifuge, surge tanks, condensate tank, and desuperheater) | 1,507,000 | 7.8 |
| Cake processing and byproduct storage (cake conveyor, steam/air heater, dryer, cyclone dust collector, fabric filter dust collectors, dryer fan, belt conveyors, bucket elevator, storage bin, vibrators, and dust fan) | 664,000 | 3.4 |
| Utilities (instrument air generation and supply, and distribution systems for process steam, water and electricity) | 265,000 | 1.4 |
| Services (buildings, shops, stores, site development, roads, railroads, and walkways) | 707,000 | 3.6 |
| Construction facilities | 931,000 | 4.8 |
| Subtotal direct investment | 19,490,000 | 100.0 |
| Engineering design and supervision | 2,151,000 | 11.0 |
| Construction field expense | 2,311,000 | 11.9 |
| Contractor fees | 978,000 | 5.0 |
| Contingency | 1,955,000 | 10.0 |
| Subtotal fixed investment | 26,727,000 | 137.0 |
| Allowance for startup and modifications | 2,679,000 | 13.7 |
| Interest during construction (8%/annum rate) | 2,153,000 | 11.0 |
| Subtotal capital investment | 31,557,000 | 161.7 |
| Land (8 acres) | 58,000 | 0.3 |
| Working capital | 1,411,000 | 7.2 |
| Total capital investment | $32,986,000 | 169.0 |

a. Basis:
Stack gas reheat to 175°F by indirect steam reheat.
Midwest plant location, average cost basis mid-1979.
Investment requirements for disposal of flyash excluded.

b. Double effect evaporator-crystallizer.

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## TABLE 9-2A. AMMONIA ABSORPTION - SCRUBBING LIQUORS SATURATED WITH AMMONIUM SULFATE - AMMONIUM SULFATE PRODUCTION TOTAL AVERAGE ANNUAL REVENUE REQUIREMENTS - REGULATED UTILITY ECONOMICS[a]

(500-MW new coal-fired power unit, 3.5% S in fuel. Dry basis; 90% $SO_2$ removal)

| | Annual quantity | Unit cost, $ | Total annual cost, $ | Percent of net annual rev. req. |
|---|---|---|---|---|
| Direct costs | | | | |
| Delivered raw material | | | | |
| Ammonia, anhydrous | 38,697 tons | 150/ton | 5,804,500 | 57.7 |
| Subtotal raw material cost | | | 5,804,500 | 57.7 |
| Conversion costs | | | | |
| Operating labor and supervision | 45,640 man-hr | 8.00/man-hr | 365,100 | 3.6 |
| Utilities | | | | |
| Steam | 706,657 MM Btu | 1.50/MM Btu | 1,060,000 | 10.5 |
| Process water | 4,025,030 M gal | 0.03/M gal | 120,800 | 1.2 |
| Electricity | 88,216,700 kWh | 0.018/kWh | 1,587,900 | 15.8 |
| Maintenance, 6% of direct investment (labor and material) | | | 1,175,000 | 11.7 |
| Analyses | | | 42,100 | 0.4 |
| Subtotal conversion costs | | | 4,350,900 | 43.2 |
| Subtotal direct costs | | | 10,155,400 | 100.9 |
| Indirect costs | | | | |
| Capital charges | | | | |
| Depreciation, interim replacement, and insurance at 4.5% of total capital investment less land and working capital | | | 1,418,800 | 14.1 |
| Average cost of capital and taxes at 10.9% of total capital investment | | | 3,438,600 | 34.2 |
| Overhead | | | | |
| Plant, 20% of conversion costs | | | 870,200 | 8.6 |
| Administrative, 10% of operating labor | | | 36,500 | 0.4 |
| Marketing, 10% of sales revenue | | | 651,000 | 6.5 |
| Subtotal indirect costs | | | 6,415,100 | 63.8 |
| Gross annual revenue requirements | | | 16,570,500 | 164.7 |
| Byproduct sales revenue | | | | |
| Ammonium sulfate | 147,957 tons | 44/ton | (6,510,100) | (64.7) |
| Subtotal byproduct sales revenue | | | (6,510,100) | (64.7) |
| Net annual revenue requirements | | | 10,060,400 | 100.0 |

| | Dollars/ton coal burned | Mills/kWh | Cents/million Btu heat input | Dollars/long ton sulfur removed |
|---|---|---|---|---|
| Equivalent net unit revenue requirement | 7.67 | 2.87 | 31.94 | 272.53 |

---

a. Basis:
Remaining life of power plant, 30 yr.
Coal burned, 1,312,500 tons/yr, 9,000 Btu/kWh.
Stack gas reheat to 175°F by indirect steam reheat.
Power unit on-stream time, 7,000 hr/yr.
Midwest plant location, 1975 revenue requirements.
Total capital investment, $31,547,000; direct investment, $19,583,000.
Investment and revenue requirement for disposal of flyash excluded.

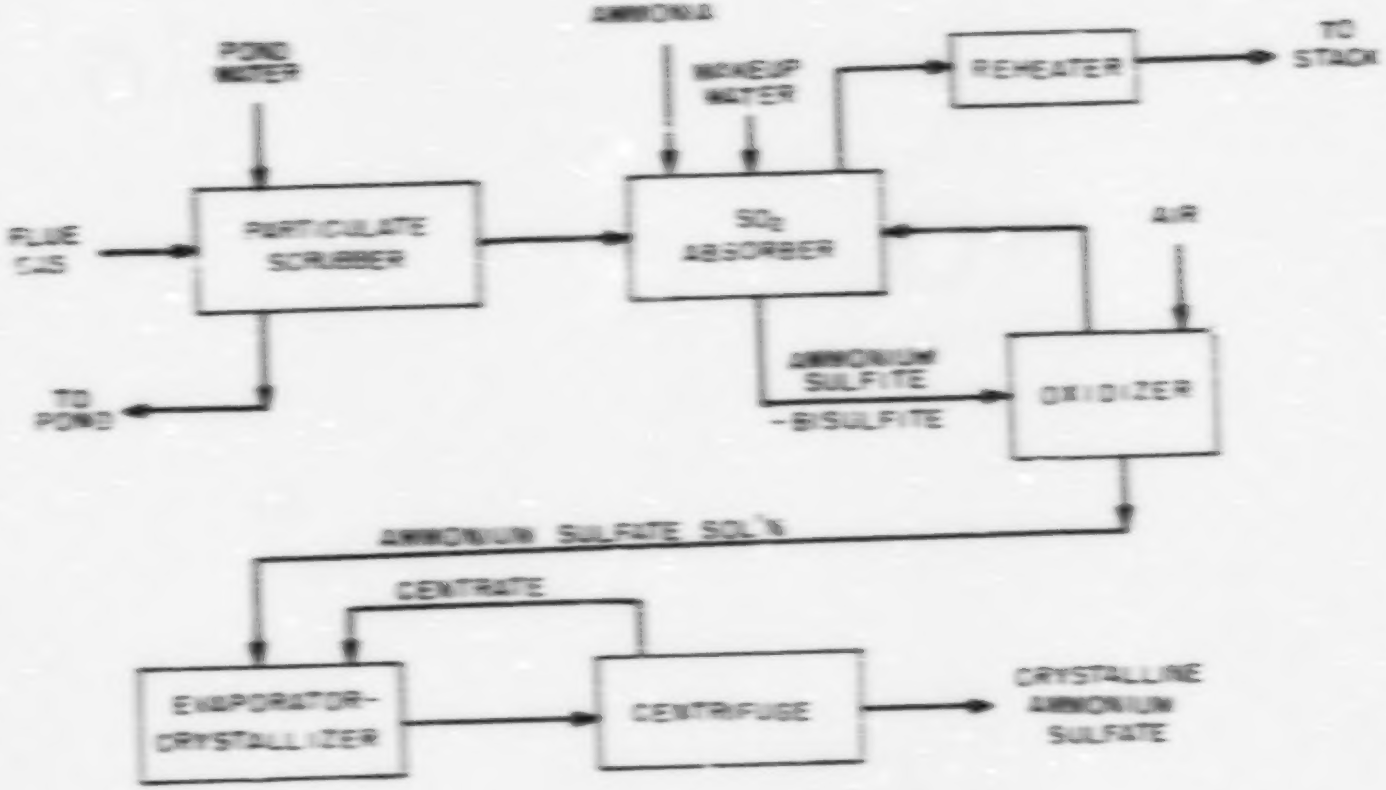
FLUE GAS
POND WATER
PARTICULATE SCRUBBER
TO POND
AMMONIA
MAKEUP WATER
$SO_2$ ABSORBER
REHEATER
TO STACK
AIR
AMMONIUM SULFITE -BISULFITE
OXIDIZER
AMMONIUM SULFATE SOL'N
CENTRATE
EVAPORATOR-CRYSTALLIZER
CENTRIFUGE
CRYSTALLINE AMMONIUM SULFATE

Figure H-2. Ammonia absorption–saturated ammonium sulfate process–ammonium sulfate production.

TABLE H-3. LIMESTONE SLURRY ABSORPTION - PONDING OF SLUDGE

SUMMARY OF ESTIMATED FIXED INVESTMENT[a]

(500-MW new coal-fired power unit, 3.5% S in fuel,
Dry basis; 90% $SO_2$ removal; onsite solids disposal)

| | Investment, $ | Percent of subtotal direct investment |
|---|---|---|
| Limestone receiving and storage (hoppers, feeders, conveyors, elevators, and bins) | 457,000 | 2.3 |
| Feed preparation (feeders, crushers, elevators, ball mills, tanks, and pumps) | 1,069,000 | 5.5 |
| Particulate scrubbers (4 scrubbers, effluent hold tanks, agitators, and pumps) | 2,308,000 | 11.8 |
| Sulfur dioxide scrubbers (4 scrubbers including mist eliminators, effluent hold tanks, agitators, and pumps) | 4,814,000 | 24.6 |
| Stack gas reheat (4 indirect steam reheaters) | 1,005,000 | 5.1 |
| Fans (4 fans including exhaust gas ducts and dampers between fan and stack gas plenum) | 3,576,000 | 18.2 |
| Calcium solids disposal (onsite disposal facilities including feed tank, agitator, slurry disposal pumps, pond, liner, and pond water return pumps) | 4,616,000 | 23.6 |
| Utilities (instrument air generation and supply system, plus distribution systems for obtaining process steam, water, and electricity from the power plant) | 80,000 | 0.4 |
| Service facilities (buildings, shops, stores, site development, roads, railroads, and walkways) | 756,000 | 3.8 |
| Construction facilities | 914,000 | 4.7 |
| Subtotal direct investment | 19,600,000 | 100.0 |
| Engineering design and supervision | 1,764,000 | 9.0 |
| Construction field expense | 2,156,000 | 11.0 |
| Contractor fees | 980,000 | 5.0 |
| Contingency | 1,960,000 | 10.0 |
| Subtotal fixed investment | 26,460,000 | 135.0 |
| Allowance for startup and modifications | 2,117,000 | 10.8 |
| Interest during construction (9%/annum rate) | 2,117,000 | 10.8 |
| Subtotal capital investment | 30,694,000 | 156.6 |
| Land (140 acres) | 490,000 | 2.5 |
| Working capital | 891,000 | 4.5 |
| Total capital investment | 32,075,000 | 163.6 |

a. Basis:
Stack gas reheat to 175°F by indirect steam reheat.
Disposal pond located 1 mile from power plant.
Midwest plant location, average cost basis mid-1975.
Investment requirements for disposal of flyash excluded.

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## TABLE B-5A. LIMESTONE SLURRY ABSORPTION - PONDING OF SLUDGE

## TOTAL AVERAGE ANNUAL REVENUE REQUIREMENTS - REGULATED UTILITY ECONOMICS[a]

(500-MW new coal-fired power unit, 3.5% S in fuel, dry basis 90% $SO_2$ removal; onsite solids disposal)

| | Annual quantity | Unit cost, $ | Total annual cost, $ | Percent of total annual rev. req. |
|---|---|---|---|---|
| **Direct costs** | | | | |
| Delivered raw material | | | | |
| Limestone | 17[illegible] tons | [illegible]/ton | [illegible] | [illegible] |
| Subtotal raw material cost | | | [illegible] | [illegible] |
| Operating costs | | | | |
| Operating labor and supervision | [illegible] man-hr | 8.[illegible] man-hr | [illegible] | [illegible] |
| Utilities | | | | |
| Steam | [illegible] MM Btu | 1.50/MM Btu | [illegible] | [illegible] |
| Process water | [illegible] M gal | 0.[illegible]/M gal | [illegible] | [illegible] |
| Electricity | 79,[illegible] kWh | 0.[illegible]/kWh | 1,[illegible] | [illegible] |
| Maintenance, [illegible]% of direct investment (labor and material) | | | 1,[illegible] | [illegible] |
| Analyses | | | [illegible] | [illegible] |
| Subtotal conversion costs | | | [illegible] | [illegible] |
| Subtotal direct costs | | | [illegible] | 46.50 |
| **Indirect costs** | | | | |
| Capital charges | | | | |
| Depreciation, interim replacement, and insurance at [illegible]% of total capital investment less land and working capital | | | 1,[illegible] | [illegible] |
| Average cost of capital and taxes at [illegible]% of total capital investment | | | 3,[illegible] | [illegible] |
| Overhead | | | | |
| Plant, [illegible]% of conversion costs | | | [illegible] | [illegible] |
| Administrative, 10% of operating labor | | | [illegible] | [illegible] |
| Subtotal indirect costs | | | [illegible] | 53.50 |
| Total annual revenue requirements | | | 10,[illegible] | 100.00 |

| | Dollars/ton coal burned | Mills/kWh | Cents/million Btu heat input | Dollars/long ton sulfur removed |
|---|---|---|---|---|
| Equivalent unit revenue requirement | [illegible] | [illegible] | [illegible] | [illegible] |

---

a. Basis:
Remaining life of power plant, 30 yr.
Coal burned, 1,51[illegible] tons/yr, 9,000 Btu/kWh.
Stack gas reheat to 175°F.
Power unit onstream time, 7,000 hr/yr.
Midwest plant location, mid-1975 revenue requirements.
Total capital investment, $[illegible]; direct investment, $[illegible].
Investment and revenue requirement for disposal of flyash excluded.

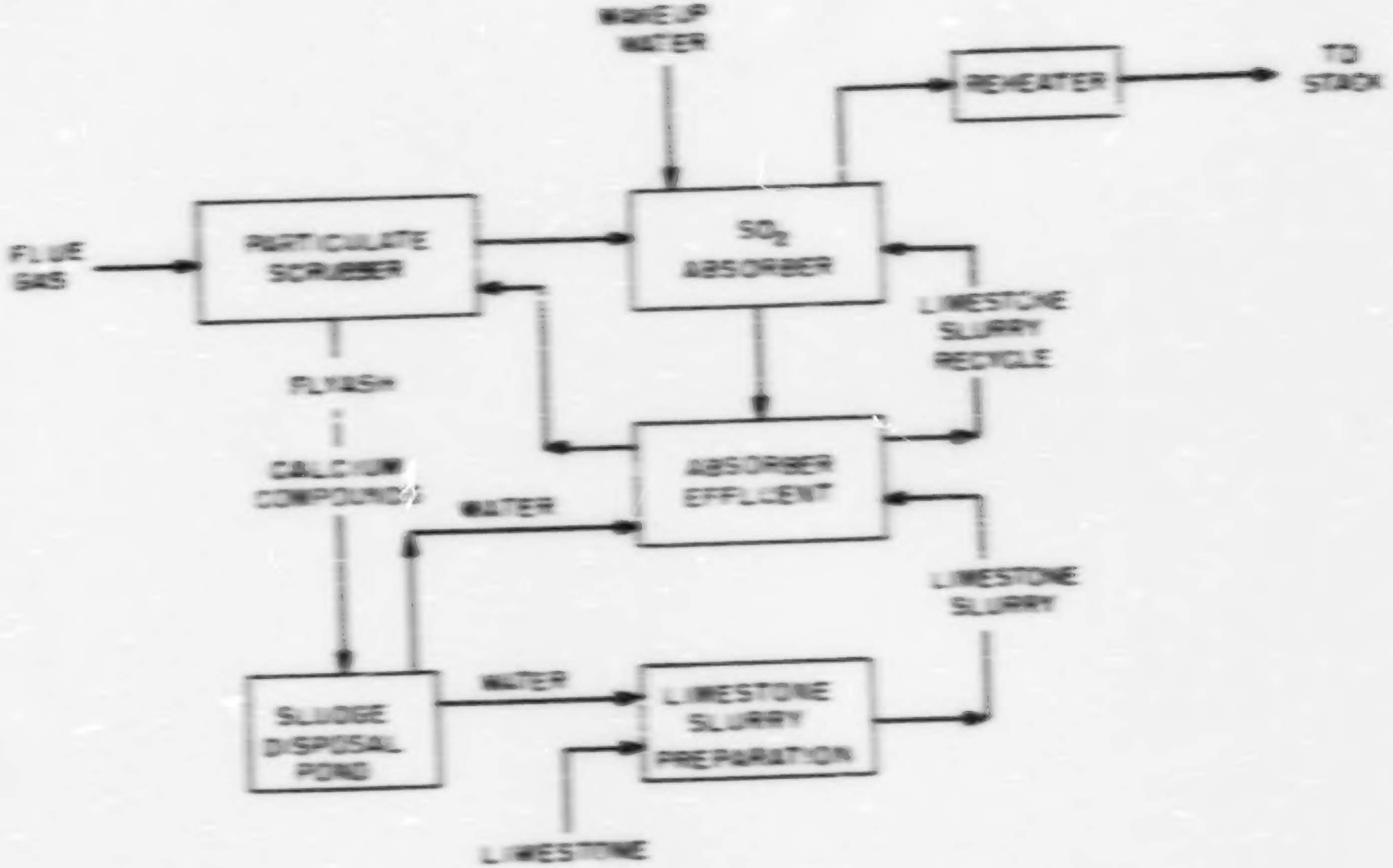
MAKEUP WATER
TO STACK
REHEATER
FLUE GAS
PARTICULATE SCRUBBER
$SO_2$ ABSORBER
LIMESTONE SLURRY RECYCLE
FLYASH
CALCIUM COMPOUNDS
ABSORBER EFFLUENT
WATER
LIMESTONE SLURRY
SLUDGE DISPOSAL POND
WATER
LIMESTONE SLURRY PREPARATION
LIMESTONE

Figure 4-3. Limestone slurry absorption— ponding of sludge.

## TABLE H-4. MAGNESIA SLURRY ABSORPTION - SULFURIC ACID PRODUCTION

## SUMMARY OF ESTIMATED FIXED INVESTMENT[a]

(500-MW new coal-fired power unit, 3.5% S in fuel. Dry basis; 90% $SO_2$ removal)

| | Investment, $ | Percent of subtotal direct investment |
|---|---|---|
| Magnesium oxide and coke receiving and storage (pneumatic conveyor and blower, hoppers, conveyors, elevators, and storage silos) | 252,000 | 1.2 |
| Feed preparation (weight feeders, conveyors, elevators, slurrying tank, agitator, and pumps) | 279,000 | 1.4 |
| Particulate scrubbers (4 scrubbers including effluent hold tanks, agitators, pumps, and flyash neutralization facilities) | 3,091,000 | 15.4 |
| Sulfur dioxide scrubbers (4 scrubbers including mist eliminators and pumps) | 2,672,000 | 13.4 |
| Stack gas reheat (4 indirect steam reheaters) | 1,003,000 | 5.0 |
| Flue gas handling (fans and duct work) | 4,119,000 | 20.6 |
| Slurry processing (screens, tanks, pumps, agitators and heating coils, centrifuges, conveyors, and elevators) | 850,000 | 4.2 |
| Drying (fluid-bed dryer, fans, combustion chamber, dust collectors, conveyors, elevators, and $MgSO_3$ storage silo) | 1,114,000 | 5.6 |
| Calcining (fluid-bed calciner, fans, weigh feeders, conveyors, elevators, waste heat boiler, dust collectors, and recycle MgO storage silo) | 1,318,000 | 6.6 |
| Sulfuric acid plant (complete contact unit for sulfuric acid production including dry gas purification system) | 2,810,000 | 14.0 |
| Sulfuric acid storage (storage and shipping facilities for 30 days' production of $H_2SO_4$) | 332,000 | 1.6 |
| Utilities (instrument air generation and supply system, fuel oil storage and supply system, and distribution systems for obtaining process steam, water, and electricity from power plant) | 319,000 | 1.6 |
| Service facilities (buildings, shops, stores, site development, roads, railroads, and walkways) | 919,000 | 4.6 |
| Construction facilities | 953,000 | 4.8 |
| Subtotal direct investment | 20,011,000 | 100.0 |
| | | |
| Engineering design and supervision | 2,201,000 | 11.0 |
| Construction field expense | 2,201,000 | 11.0 |
| Contractor fees | 1,001,000 | 5.0 |
| Contingency | 2,001,000 | 10.0 |
| Subtotal fixed investment | 27,415,000 | 137.0 |
| | | |
| Allowance for startup and modifications | 2,742,000 | 13.7 |
| Interest during construction (9%/annum rate) | 2,193,000 | 10.9 |
| Subtotal capital investment | 32,350,000 | 161.6 |
| | | |
| Land (8 acres) | 28,000 | 0.1 |
| Working capital | 1,181,000 | 5.9 |
| | | |
| Total capital investment | 33,559,000 | 167.6 |

a. Basis:
Stack gas reheat to 175°F by indirect steam reheat.
Midwest plant location, average cost basis mid-1975.
Investment requirements for disposal of flyash excluded.

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## TABLE B-6A. MAGNESIA SLURRY ABSORPTION - SULFURIC ACID PRODUCTION

## TOTAL AVERAGE ANNUAL REVENUE REQUIREMENTS - REGULATED UTILITY ECONOMICS[a]

(500-MW new coal-fired power unit, 3.5% S in fuel; dry basis; 90% [illegible] removal)

| | Annual quantity | Unit cost, $ | Total annual cost, $ | Percent of total annual rev. req. |
|---|---|---|---|---|
| **Direct costs** | | | | |
| Delivered raw materials | | | | |
| Lime (1st stage neutralization) | 134 tons | [illegible] | [illegible] | [illegible] |
| Magnesium oxide (98%) | [illegible] tons | [illegible] | [illegible] | [illegible] |
| Coke | [illegible] tons | [illegible] | [illegible] | [illegible] |
| Catalyst | [illegible] liters | [illegible] | [illegible] | [illegible] |
| Subtotal raw materials cost | | | [illegible] | [illegible] |
| Conversion costs | | | | |
| Operating labor and supervision | [illegible] man-hr | [illegible] | [illegible] | [illegible] |
| Utilities | | | | |
| Fuel oil (No. 6) | [illegible] gal | [illegible] | [illegible] | [illegible] |
| Steam | [illegible] | [illegible] | [illegible] | [illegible] |
| Heat credit | [illegible] | [illegible] | [illegible] | [illegible] |
| Process water | [illegible] gal | [illegible] | [illegible] | [illegible] |
| Electricity | [illegible] kWh | [illegible] | [illegible] | [illegible] |
| Maintenance, [illegible]% of direct investment (labor and material) | | | [illegible] | [illegible] |
| Analyses | | | [illegible] | [illegible] |
| Subtotal conversion costs | | | [illegible] | [illegible] |
| Subtotal direct costs | | | [illegible] | [illegible] |
| **Indirect costs** | | | | |
| Capital charges | | | | |
| Depreciation, interim replacements, and insurance at [illegible]% of total capital investment less land and working capital | | | [illegible] | [illegible] |
| Average cost of capital and taxes at [illegible]% of total capital investment | | | [illegible] | [illegible] |
| Overhead | | | | |
| Plant, [illegible]% of conversion costs | | | [illegible] | [illegible] |
| Administrative, [illegible]% of operating labor | | | [illegible] | [illegible] |
| Marketing, [illegible]% of sales revenue | | | [illegible] | [illegible] |
| Subtotal indirect costs | | | [illegible] | [illegible] |
| Gross annual revenue requirements | | | [illegible] | [illegible] |
| **Byproduct sales revenue** | | | | |
| Sulfuric acid (98%) | [illegible] tons | [illegible] | [illegible] | [illegible] |
| Subtotal byproduct sales revenue | | | [illegible] | [illegible] |
| Total annual revenue requirements | | | [illegible] | [illegible] |

| | Dollars/ton coal burned | Mills/kWh | Cents/million Btu heat input | Dollars/ton sulfur removed |
|---|---|---|---|---|
| Equivalent unit revenue requirement | [illegible] | [illegible] | [illegible] | [illegible] |

---

a. Basis
Remaining life of power plant, [illegible] yr.
Coal burned, [illegible] tons/yr, [illegible] Btu/kWh.
Stack gas reheat to 175°F by indirect steam reheat.
Power unit onstream time, [illegible] hr/yr.
Midwest plant location, [illegible] revenue requirements.
Total capital investment, $[illegible]; direct investment, $[illegible].
Investment and revenue requirement for disposal of flyash excluded.

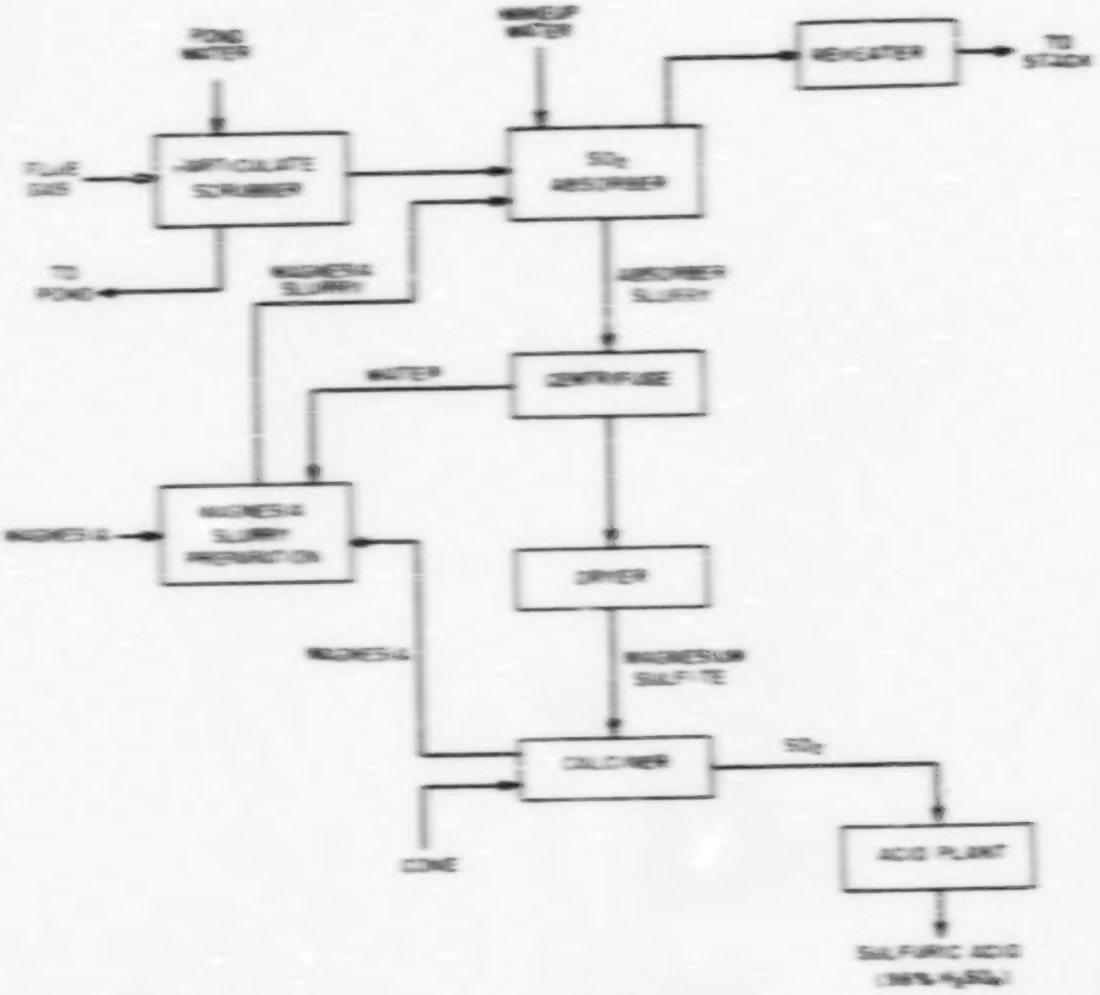
POND WATER
FLUE GAS
PARTICULATE SCRUBBER
TO POND
MAKEUP WATER
SO2 ABSORBER
REHEATER
TO STACK
MAGNESIA SLURRY
ABSORBER SLURRY
WATER
CENTRIFUGE
MAGNESIA
MAGNESIA SLURRY PREPARATION
DRYER
MAGNESIUM SULFITE
MAGNESIA
CALCINER
COKE
SO2
ACID PLANT
SULFURIC ACID (98% H2SO4)

Figure H-4. Magnesia slurry absorption—sulfuric acid production.

## TABLE H-5. SODIUM SULFITE ABSORPTION - SULFURIC ACID PRODUCTION

## SUMMARY OF ESTIMATED FIXED INVESTMENT[a]

(500-MW new coal-fired power unit, 3.5% S in fuel, dry basis; 90% $SO_2$ removal)

| | Investment, $ | Percent of subtotal direct investment |
|---|---|---|
| Soda ash and antioxidant receiving, storage, and preparation (pneumatic conveyor and blower, feeders, mixing tank, agitator, and pumps) | 269,000 | 1.2 |
| Particulate scrubbers (4 scrubbers including effluent hold tanks, agitators, pumps, and flyash neutralization facilities) | 3,091,000 | 13.4 |
| Sulfur dioxide scrubbers (4 scrubbers including mist eliminators and pumps) | 4,559,000 | 19.8 |
| Stack gas reheat (4 indirect steam reheaters) | 1,003,000 | 4.4 |
| Flue gas handling (fans and duct work) | 4,174,000 | 18.2 |
| Purge treatment (refrigeration system, chiller-crystallizer, feed coolers, centrifuge, rotary dryer, steam/air heater, fan, dust collectors, feeders, tanks, agitators, pumps, conveyors, elevator, and bins) | 1,635,000 | 7.1 |
| Sulfur dioxide regeneration (evaporator-crystallizers, heaters, condensers, strippers, desuperheater, tanks, agitators, and pumps) | 3,182,000 | 13.8 |
| Sulfuric acid plant (complete contact unit for sulfuric acid production) | 2,659,000 | 11.5 |
| Sulfuric acid storage (storage and shipping facilities for 30 days' production of $H_2SO_4$) | 313,000 | 1.4 |
| Utilities (instrument air generation and supply system, and distribution systems for obtaining process steam, water, and electricity from power plant) | 230,000 | 1.0 |
| Service facilities (buildings, shops, stores, site development, roads, railroads, and walkways) | 776,000 | 3.4 |
| Construction facilities | 1,096,000 | 4.8 |
| Subtotal direct investment | 22,985,000 | 100.0 |
| | | |
| Engineering design and supervision | 2,528,000 | 11.0 |
| Construction field expense | 2,528,000 | 11.0 |
| Contractor fees | 1,149,000 | 5.0 |
| Contingency | 2,298,000 | 10.0 |
| Subtotal fixed investment | 31,496,000 | 137.0 |
| | | |
| Allowance for startup and modifications | 3,149,000 | 13.7 |
| Interest during construction (9%/annum rate) | 2,512,000 | 10.9 |
| Subtotal capital investment | 37,154,000 | 161.6 |
| | | |
| Land (8 acres) | 28,000 | 0.1 |
| Working capital | 1,385,000 | 6.0 |
| | | |
| Total capital investment | 38,567,000 | 167.7 |

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a. Basis:
Stack gas reheat to 175°F by indirect steam reheat.
Midwest plant location, average cost basis mid-1975.
Investment requirements for disposal of flyash excluded.

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## TABLE H-5A. SODIUM SULFITE ABSORPTION – SULFURIC ACID PRODUCTION

## TOTAL AVERAGE ANNUAL REVENUE REQUIREMENTS – REGULATED UTILITY ECONOMICS[a]

(500-MW new coal-fired power unit, 3.5% S in fuel; dry basis; 90% $SO_2$ removal)

| | Annual quantity | Unit cost, $ | Total annual cost, $ | Percent of total annual rev. req. |
|---|---|---|---|---|
| Direct costs | | | | |
| Delivered raw materials | | | | |
| Lime (1st stage neutralization) | 134 tons | 40.00/ton | 5,400 | 0.05 |
| Soda ash | 9,300 tons | 52.00/ton | 483,600 | 4.36 |
| Antioxidant | 317,100 lb | 2.70/lb | [illegible] | [illegible] |
| Catalyst | 1,800 liters | [illegible]/liter | [illegible] | 0.03 |
| Subtotal raw materials cost | | | [illegible] | [illegible] |
| Conversion costs | | | | |
| Operating labor and supervision | 45,900 man-hr | 8.00/man-hr | 367,200 | 3.29 |
| Utilities | | | | |
| Steam | 1,755,500 MM Btu | [illegible]/MM Btu | [illegible] | 23.61 |
| Process water | 11,672,500 M gal | [illegible]/M gal | [illegible] | 0.09 |
| Electricity | 79,536,000 kWh | 0.019/kWh | 1,511,200 | 13.55 |
| Maintenance, 8% of direct investment (labor and material) | | | 1,770,400 | 15.9 |
| Analyses | | | 108,[illegible] | 0.97 |
| Subtotal conversion costs | | | [illegible] | [illegible] |
| Subtotal direct costs | | | [illegible] | 65.8[illegible] |
| Indirect costs | | | | |
| Capital charges | | | | |
| Depreciation, interim replacement, and insurance at 5.9% of total capital investment less land and working capital | | | 1,671,200 | 14.98 |
| Average cost of capital and taxes at 10.9% of total capital investment | | | 4,0[illegible] | 35.9 |
| Overhead | | | | |
| Plant, 50% of conversion costs | | | [illegible] | 11.[illegible] |
| Administrative, 10% of operating labor | | | 36,700 | 0.33 |
| Marketing, 10% of sales revenue | | | 4[illegible] | 4.[illegible] |
| Subtotal indirect costs | | | 7,791,800 | 69.9[illegible] |
| Gross annual revenue requirement | | | 16,570,500 | 150.[illegible] |
| Byproduct sales revenue | | | | |
| Sodium sulfate | 13,000 tons | 24.00/ton | (312,000) | (2.79) |
| Sulfuric acid (98%) | 103,5[illegible] tons | 40.00/ton | ([illegible]) | ([illegible]) |
| Subtotal byproduct sales revenue | | | ([illegible]) | ([illegible]) |
| Total annual revenue requirements | | | 11,153,500 | 100.00 |

| | Dollars/ton coal burned | Mills/kWh | Cents/million Btu heat input | Dollars/long ton sulfur removed |
|---|---|---|---|---|
| Equivalent unit revenue requirement | 8.49 | 3.19 | 35.[illegible] | [illegible] |

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a. Basis:
Remaining life of power plant, 30 yr.
Coal burned, 1,312,500 tons/yr, 9,000 Btu/kWh.
Stack gas reheat to 175°F by indirect steam reheat.
Power unit on-stream time, 7,000 hr/yr.
Midwest plant location, 1977 revenue requirements.
Total capital investment, $37,154,000; direct investment, $22,[illegible],000.
Investment and revenue requirement for disposal of flyash excluded.

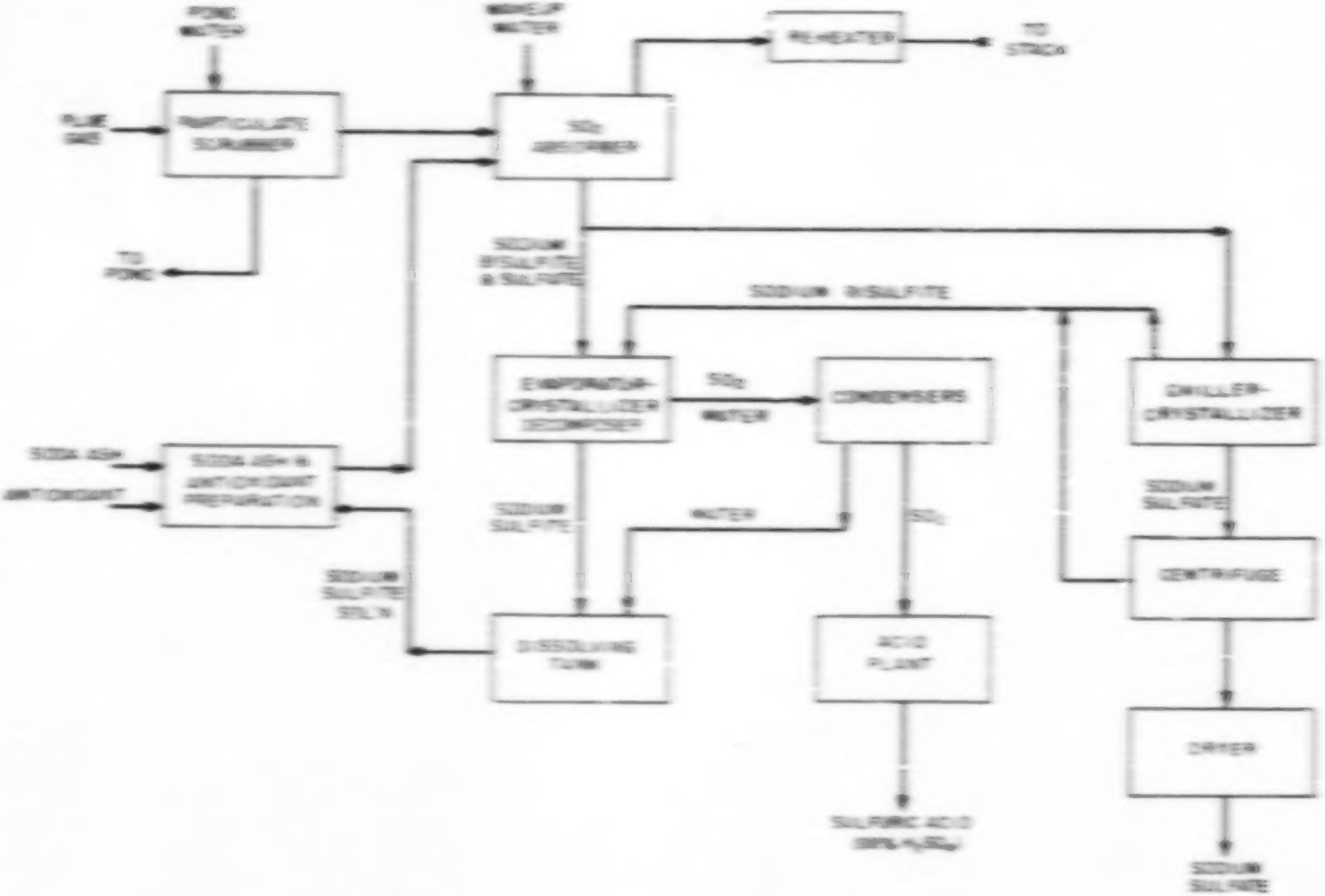
FLUE GAS
POND WATER
PARTICULATE SCRUBBER
TO POND
MAKEUP WATER
SO2 ABSORBER
REHEATER
TO STACK
SODA ASH
ANTIOXIDANT
SODA ASH & ANTIOXIDANT PREPARATION
SODIUM BISULFITE & SULFATE
SODIUM BISULFITE
EVAPORATOR-CRYSTALLIZER DECOMPOSER
SO2
WATER
CONDENSERS
CHILLER-CRYSTALLIZER
SODIUM SULFITE
WATER
SO2
SODIUM SULFITE SOL'N
DISSOLVING TANK
ACID PLANT
SULFURIC ACID (98% H2SO4)
SODIUM SULFATE
CENTRIFUGE
DRYER
SODIUM SULFATE

Figure 4-5. Sodium sulfite absorption—sulfuric acid production.